K-1647
(NASA-CR-54482)

AEC RESEARCH AND DEVELOPMENT REPORT

This document contains Restricted Data relating to Civilian Applications of Atomic Energy.

FINAL REPORT FOR FY 1965 ON TUNGSTEN-URANIUM DIOXIDE MATERIALS FOR NASA

PART I:
Preparation of High Purity Uranium Oxide Powders (U)

PART II:
Cladding and Joining of Tungsten Cermets by Plasma Spraying (U)

PART III:
Tungsten Coating of Uranium Dioxide Particles

AUTHORS:

W. L. Cochran
R. G. Knight
F. S. Stanley

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION

Operating the

U. S. Government Agencies and ~~Contractors Only~~

OAK RIDGE GASEOUS DIFFUSION PLANT • OAK RIDGE NATIONAL LABORATORY
OAK RIDGE Y-12 PLANT • PADUCAH GASEOUS DIFFUSION PLANT

For the Atomic Energy Commission
Under U.S. Government Contract W7405 eng 26

Printed in USA. Charge: $2.45 Available from the

U. S. Atomic Energy Commission
Division of Technical Information Extension
P. O. Box 62
Oak Ridge, Tennessee 37831

Please direct to the same address inquiries covering the procurement of other classified AEC reports.

C67-1331

Date of Issue: October 11, 1965 Report Number: K-1647
(NASA-CR-54482)

Subject Category: NUCLEAR REACTORS
FOR ROCKET
PROPULSION

FINAL REPORT FOR FY 1965 ON TUNGSTEN-URANIUM DIOXIDE MATERIALS FOR NASA

Part I: Preparation of High Purity Uranium Oxide Powders (U)

Part II: Cladding and Joining of Tungsten Cermets by Plasma Spraying (U)

Part III: Tungsten Coating of Uranium Dioxide Particles [U]

By

W. L. Cochran
R. G. Knight
F. S. Stanley

Engineering Development Department
Technical Division

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Materials and Structures Division
Robert M. Caves
Richard E. Gluyas

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

A B S T R A C T

Part I: PREPARATION OF HIGH PURITY URANIUM OXIDE POWDERS (U)

Several uranium oxide fuel materials were prepared for evaluation by the NASA Lewis Research Center. Included was a 2-pound sample of plasma jet spheroidized, 30- to 60-micron uranium dioxide of precisely controlled stoichiometry containing less than 50 ppm. metallic impurities. Six 1-pound samples of 30- to 60-micron uranium dioxide were prepared which contained calcium oxide, thorium oxide, or yttrium oxide stabilizing agents in solid solution. These powders were coated with 8 to 10 microns of tungsten by hydrogen reduction of tungsten hexafluoride in a fluidized bed. Seven 1-pound samples of 30- to 60-micron uranium dioxide containing various concentrations of yttrium oxide in solid solution were also prepared. Finally, a 1-pound sample of less than 5-micron uranium dioxide containing 10 mole percent yttrium oxide was produced.

Part II: CLADDING AND JOINING OF TUNGSTEN CERMETS BY PLASMA SPRAYING (U)

Procedures were developed for applying metallurgically bonded tungsten coatings to the edges of tungsten-uranium dioxide cermet fuel elements. These coatings were effective in reducing the uranium dioxide loss in high temperature tests at NASA.

Part III: TUNGSTEN COATING OF URANIUM DIOXIDE PARTICLES [U]

Of several techniques examined for producing a halide free tungsten coating on 30- to 60-micron uranium dioxide powder, the most promising were (a) vacuum evaporation of tungsten using electron beam heating, and (b) electrostatically bonding fine tungsten trioxide powder onto the uranium dioxide, followed by conversion to tungsten by hydrogen reduction.

TABLE OF CONTENTS

TABLE OF CONTENTS (Contd.)

TABLE OF CONTENTS (Contd.)

LIST OF TABLES

LIST OF TABLES (Contd.)

LIST OF TABLES (Contd.)

LIST OF FIGURES

LIST OF FIGURES (Contd.)

LIST OF FIGURES (Contd.)

INTRODUCTION

This is a completion report on work performed for the NASA Lewis Research Center from July 1, 1964, through June 30, 1965, on Part I: Preparation of High Purity Uranium Oxide Powders; Part II: Cladding and Joining of Tungsten Cermets by Plasma Spraying; and Part III: Tungsten Coating of Uranium Dioxide Particles. For economy, the descriptions of these three studies have been combined into a single report. To aid the reader, the results of these investigations are presented in separate and independent write-ups which comprise the three main parts of the report. A summary of the work is presented at the beginning of each section.

PART I

PREPARATION OF HIGH PURITY URANIUM OXIDE POWDERS (U)

By

W. L. Cochran
R. G. Knight
F. S. Stanley

Engineering Development Department
Technical Division

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

(Identification C-25101A)

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Materials and Structures Division
Richard E. Gluyas

Part I: PREPARATION OF HIGH PURITY URANIUM OXIDE POWDERS

SUMMARY

A 2-pound sample of 98% spheroidized, 30- to 60-micron uranium dioxide has been prepared by a plasma jet technique (task 1). Ultrahigh purity urano-uranic oxide was processed twice through a dc. plasma arc to obtain the desired stoichiometry and spheroidization; and after sizing, the plasma jet product was processed on a vibratory inclined plane to separate the spheroids from the irregularly shaped particles. The final product had an oxygen-to-uranium ratio of 2.000 and contained less than 50 ppm. detectable metallics.

A series of tests has been performed in an effort (task 5) to scale up the plasma jet spheroidization process and to reduce the product cost. The starting material for this work was uranium trioxide prepared by fluid-bed denitration, a process employed on a commercial scale in AEC feed material plants at low cost. With minor modifications, this process could be employed to yield an ultrahigh purity product. Use of the less frangible urano-uranic oxide prepared from this material resulted in improved penetration of the powder into the turbulent plasma stream. This improved penetration, combined with the use of a higher energy helium plasma, permitted a six-fold increase in throughput, plus a sizable gain in spheroidization efficiency. These improvements should produce a reduction in unit cost of at least an order of magnitude. It should be noted, however, that the effort on this task was terminated before methods had been developed to control the stoichiometry for the new processing conditions.

Since November, 1964, priority has been placed on the preparation of 30- to 60-micron uranium dioxide containing stabilizing additives, such as calcium oxide, yttrium oxide, or thorium oxide, in solid solutions (task 6). After blending and compacting at 75,000 psi., the compacts were furnaced, including reduction in hydrogen at 1100°C. to obtain the desired stoichiometry, followed by extended treatment at 2200°C. to achieve the solid solution by diffusion. The early batches were furnaced either at NASA or at the Y-12 Plant; however, a tungsten resistance furnace has been constructed to provide this capability at the ORGDP. After sintering, the stabilized uranium dioxide was ground and screened to the desired 30- to 60-micron size range. For early batches, comminution was achieved by grinding in a mortar and pestle, followed by size reduction in a tungsten-lined fluid energy mill. Later batches were ground between orbiting tungsten plates.

The first series of stabilized uranium dioxide powders were then coated with an 8- to 10-micron layer of tungsten by the hydrogen reduction of tungsten hexafluoride in a fluidized bed. Limited availability of suitable powders for test purposes, plus a demanding schedule, permitted only a cursory attempt to lower the fluoride content of the coated product, with the result that the tungsten-coated powders shipped to NASA varied

considerably in fluoride content.

Detectable metallic impurities in the tungsten-coated powder were in the 20 to 40 ppm. range. The impurity level in the coated product was surprisingly low when compared with the impurities in the ceramic-grade oxide used as starting material or with the impurities in the ground and screened intermediates. It is possible that fine, particulate impurities were elutriated from the uranium dioxide powder during reduction in the fluidized bed, i.e., prior to coating, and that this may account for the low impurity level in the final product.

Environmental tests conducted at NASA indicated that the additive, yttria, was better than either thoria or calcia for the prevention of uranium loss at elevated temperatures; and for this reason, an additional series of powders having different yttria concentrations, between 2-1/2 and 15%, was prepared for evaluation at NASA. For these powders, the metallic impurity contents were between 19 and 143 ppm., while the carbon contents varied from 6 to 21 ppm. The fine particle by-products which represent a substantial percentage of the starting material also met the purity specifications. The maximum detectable metallics and carbon content were 287 and 25 ppm., respectively.

A number of exploratory studies have been undertaken to develop a method for the preparation of ultrafine uranium dioxide powders. The original objective was to prepare powder with an average size below 5 microns and with a sizable percentage below 1 micron. This objective was later changed to include preparation of powder with an average size in the 5- to 10-micron range with a sharp distribution. Included in the investigation were three grinding methods: rod milling, fluid energy milling, and grinding between orbiting tungsten plates. All appear capable of producing material in the desired range. Other methods which showed promise include vaporization-condensation in the plasma jet and hydration-dehydration of uranium trioxide. Some sizing of the product will probably be required for any of these techniques if a sharp size distribution is needed. Ultrasonic dispersion, followed by sedimentation in liquid media, has been briefly tested for the sizing operation.

INTRODUCTION

This program is a continuation and extension of the high purity uranium dioxide fuel development activities conducted at the Oak Ridge Gaseous Diffusion Plant during fiscal year 1964. This program has been aimed at the development of practical methods for the preparation of uranium oxide powders of controlled purity, particle size, and particle shape. Samples of various powders with closely defined characteristics were prepared for submission to NASA for testing and evaluation in connection with materials research for the tungsten, water-moderated, nuclear rocket concept under study at the NASA Lewis Research Center.

The original objectives called for development of methods for preparation of uranium oxides of various purity and particle size requirements with closely controlled oxygen-to-uranium ratios. Reasonably economical processes were to be established for the preparation of relatively large quantities, e.g., 100 pounds, of 30- to 60-micron spheroidal uranium dioxide. In addition, methods were to be developed for preparing micronized uranium dioxide and for characterizing its particle size distribution. The specific objectives are spelled out in more detail in the Introductions to the six tasks into which this program has been divided.

For the first 4 months of fiscal year 1965, emphasis was placed on the development and scale-up of a plasma jet process for the preparation of spheroidized, 30- to 60-micron uranium dioxide. In November, 1964, a major change in emphasis occurred. Priority was placed on the preparation of tungsten-coated, 30- to 60-micron uranium dioxide containing calcium oxide, yttrium oxide, and thorium oxide additives which would stabilize the uranium dioxide and prevent fuel loss at the proposed operating temperatures of the nuclear rocket engines. In April, 1965, emphasis was placed on the preparation of 30- to 60-micron uranium dioxide containing various concentrations of yttrium oxide additive.

HIGH PURITY, STOICHIOMETRIC URANIUM DIOXIDE (TASK 1)

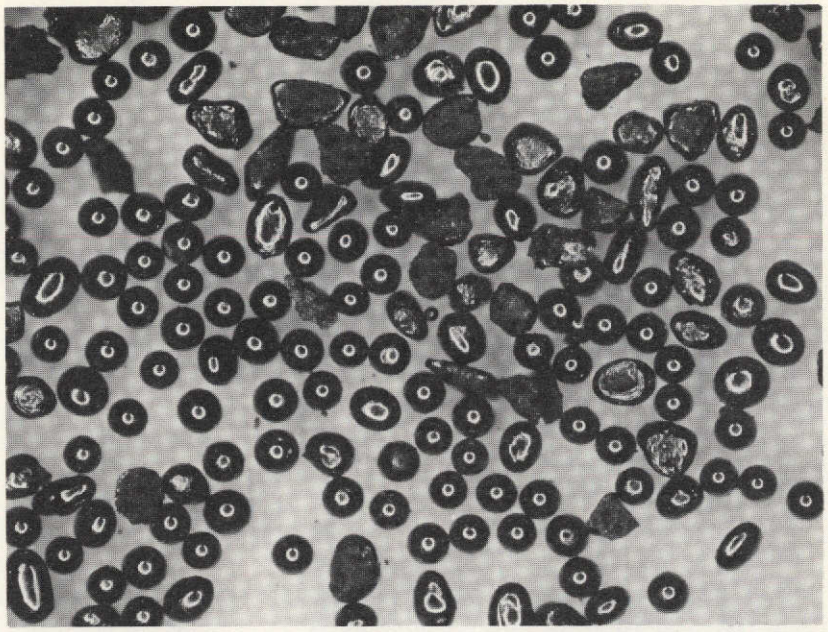
A 2-pound sample of high purity, 98% spheroidized, 30- to 60-micron uranium dioxide powder was prepared and shipped in completion of task 1. A photomicrograph of this spheroidized product at 72× magnification is presented in figure 1, and a summary of the spectroscopic and chemical analyses on the 2-pound sample is shown in table I. A tabulation of the limits of detection for the elements sought in the spectrochemical analysis appears in table II.

The 2-pound sample was produced by techniques developed at the Oak Ridge Gaseous Diffusion Plant. Urano-uranic oxide (U_3O_8), prepared in the Works Laboratory by the uranium peroxide precipitation route, was fed through a hollow tungsten cathode into an argon plasma generated by a reactor-mounted M-4 plasma torch. Hydrogen, introduced with the powder to be spheroidized, provided a reducing atmosphere, and two passes of the powder through the system produced the desired oxygen-to-uranium ratio of 2.000 to 1.

Impurities were minimized in the product by the following procedures:

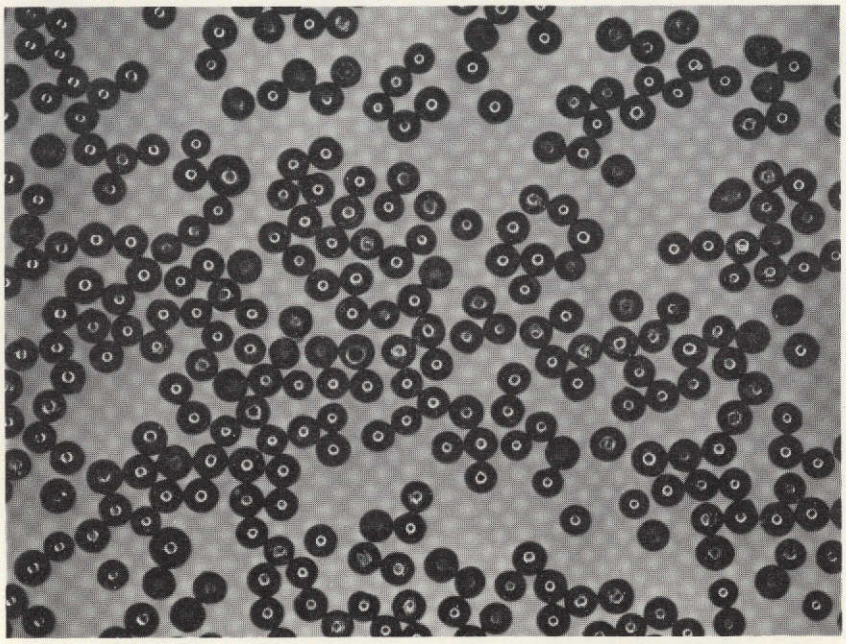
1. Using the ultrahigh purity feed material.

2. Tungsten coating the plasma jet front electrode. The tungsten vapor plating was done at ORGDP by the hydrogen reduction of tungsten hexafluoride. The tungsten coating applied this way protects the front electrode from erosion and prevents copper contamination in the product. Since the uranium dioxide will eventually be mixed with tungsten in fuel element fabrication, tungsten is an acceptable contaminant. Hourly electrode inspection was adequate to detect erosion spots on



Magnification - 100X

Before Upgrading



Magnification - 100X

After Upgrading

PHOTOMICROGRAPH OF SPHEROIDIZED, STOICHIOMETRIC, 30- TO 60-MICRON URANIUM DIOXIDE

Figure 1

TABLE I

COMPOSITE ANALYTICAL RESULTS ON THE 2-POUND BATCH OF SPHEROIDAL, STOICHIOMETRIC, 30- TO 60-MICRON URANIUM DIOXIDE

Analysis	Impurity Content
Spectrochemical, ppm.*	5
Aluminum	5
Silver	1
Chromium	3
Copper	3
Iron	10
Magnesium	7
Nickel	6
Silicon	6
Total	41
Carbon, ppm.	28
Tungsten, ppm.	275
Oxygen-To-Uranium Ratio	2.000
Percentage Spheroidized	> 98

* A listing of elements sought by spectrochemical analysis, together with the limit of detection, is presented in table II.

TABLE II

LIMIT OF DETECTION FOR SPECTROCHEMICAL ANALYSIS OF URANIUM DIOXIDE

Element	Limit of Detection, ppm.
Aluminum	< 1
Antimony	< 15
Arsenic	< 30
Barium	< 10
Beryllium	< 1
Bismuth	< 1
Boron	< 1
Cadmium	< 1
Calcium	< 1
Chromium	< 3
Cobalt	< 1
Copper	< 1
Germanium	< 1
Gold	< 1
Indium	< 3
Iron	< 5
Lead	< 3
Lithium	< 1
Magnesium	< 1
Manganese	< 1
Nickel	< 2
Phosphorus	< 50
Potassium	< 5
Silicon	< 1
Silver	< 1
Sodium	< 1
Thallium	< 2
Tin	< 1
Zinc	< 20

the tungsten plate in time to prevent copper contamination.

3. Careful handling of the product through the screening and upgrading steps of the process. Contact with any material which would contaminate the powder was avoided by conducting these operations in a glove box.

After two passes through the plasma jet, the product consisted of a mixture of spheroids and irregularly shaped particles. The nonspheroidal particles were separated from the spheroidal particles by a vibrating inclined plane separator that carried the irregular particles to the top by vibratory motion and permitted the spheroids to roll off the bottom. During final separation, frequent microscopic examination of the product was used to assure the desired degree of spheroidicity. The separation process required considerable attention, since the separation efficiency was highly dependent on the powder feed rate and on the percentage of spheroids in the feed material. The upgrading operation was performed in a dry box which was gas blanketed to minimize contamination with particulate matter. Even with these precautions, it was necessary to inspect the material visually and to remove visible particulate contaminants before the purity level, shown in table I, was reached. It has been observed that contamination seems to be a function of in-process time; and at higher throughput levels, the contamination problem is less severe.

The specifications on stoichiometry, spheroidicity, purity, and particle size were met in the 2-pound sample; thus, this task was completed.

URANIUM DIOXIDE WITH ADDED IMPURITIES (TASK 2)

In the original work statement, the objective for this project was defined as the preparation of highly spheroidized, ultrahigh purity, stoichiometric uranium dioxide powder containing impurities, such as nickel, carbon, nitrogen, fluorine, or sulfur, which have deliberately been added in amounts ranging from 50 to 1,000 ppm. These added impurities were to be distributed uniformly through the uranium dioxide. The original plans called for these impurities to be added by an appropriate technique and then to be distributed throughout the uranium dioxide by diffusion while the particles were being spheroidized in the plasma jet. No work was performed on this task because of a redirection in the program effort by NASA.

It should be noted that this is not an easy task. Use of the plasma spheroidization technique just described (task 1) at its present stage of development would probably prove too costly, and the effect of plasma jet temperature on the fate of each impurity would have to be determined. Thus, alternative approaches should be considered before work of this nature is undertaken, and powders have not been prepared due to emphasis on other tasks.

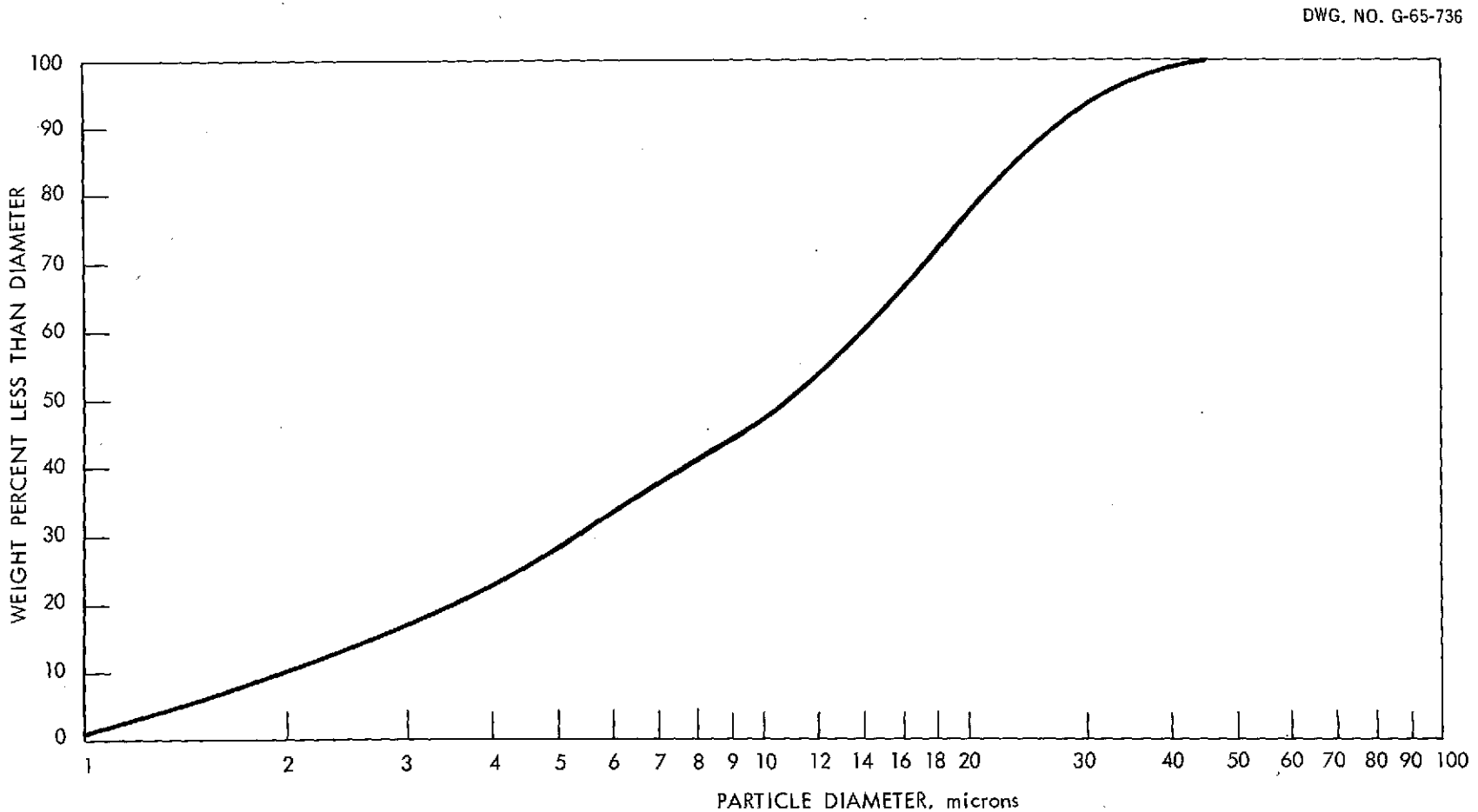
PROCESS FOR ULTRAFINE URANIUM DIOXIDE (TASK 3)

The original work statement defined this task as the development of a process for the preparation of ultrafine uranium dioxide with an average size less than 5 microns, with a substantial portion in the 1-micron range. In February, 1965, the work was redirected at the request of the NASA Project Manager toward the production of powder between 5 and 10 microns in size which might possibly be vapor-plated with tungsten in a fluidized bed, but this request was later revised and was limited to the preparation of a pound lot of less than 2-micron powder containing 10 mole percent yttria in solid solution. The techniques developed should provide small samples of powder with high purity levels. Five techniques were explored for preparing fine powders: (a) three grinding methods, (b) comminution by hydration-dehydration of uranium trioxide, and (c) preparation of fine uranium dioxide by vaporization-condensation in the plasma jet.

The three mechanical methods involve rod milling, fluid energy milling, and grinding between orbiting tungsten plates. In preparing the 30- to 60-micron uranium dioxide by any of these techniques (task 6), approximately 50% of the feed was lost as undersize; i.e., minus 400-mesh. The particle size distributions by Micromerograph of typical fine fractions are presented in figures 2 and 3. Further size reduction could undoubtedly be achieved by increasing the milling time. The orbiting tungsten plates were most effective in the earlier phase of the grinding operation, while the fluid energy mill was preferred for final size reduction.

Another technique which has been explored briefly is comminution by hydration-dehydration of uranium trioxide. Results of a series of test runs on samples of uranium trioxide prepared by different methods are summarized in table III, and the particle size distributions before and after treatment of a typical sample are presented in figure 4. It can be noted that the degree of comminution is not sufficient to meet the original goal of 1-micron powder; however, hydration and reduction may be a very satisfactory method for the production of a material in the 5- to 10-micron range. The hydration-dehydration of uranium trioxide appears to be a promising method for comminution of pure uranium oxides. There might be serious complications in applying this technique to the size reduction of uranium oxides containing additives in solid solution, however, because of the requirements for stoichiometry and density of the final product.

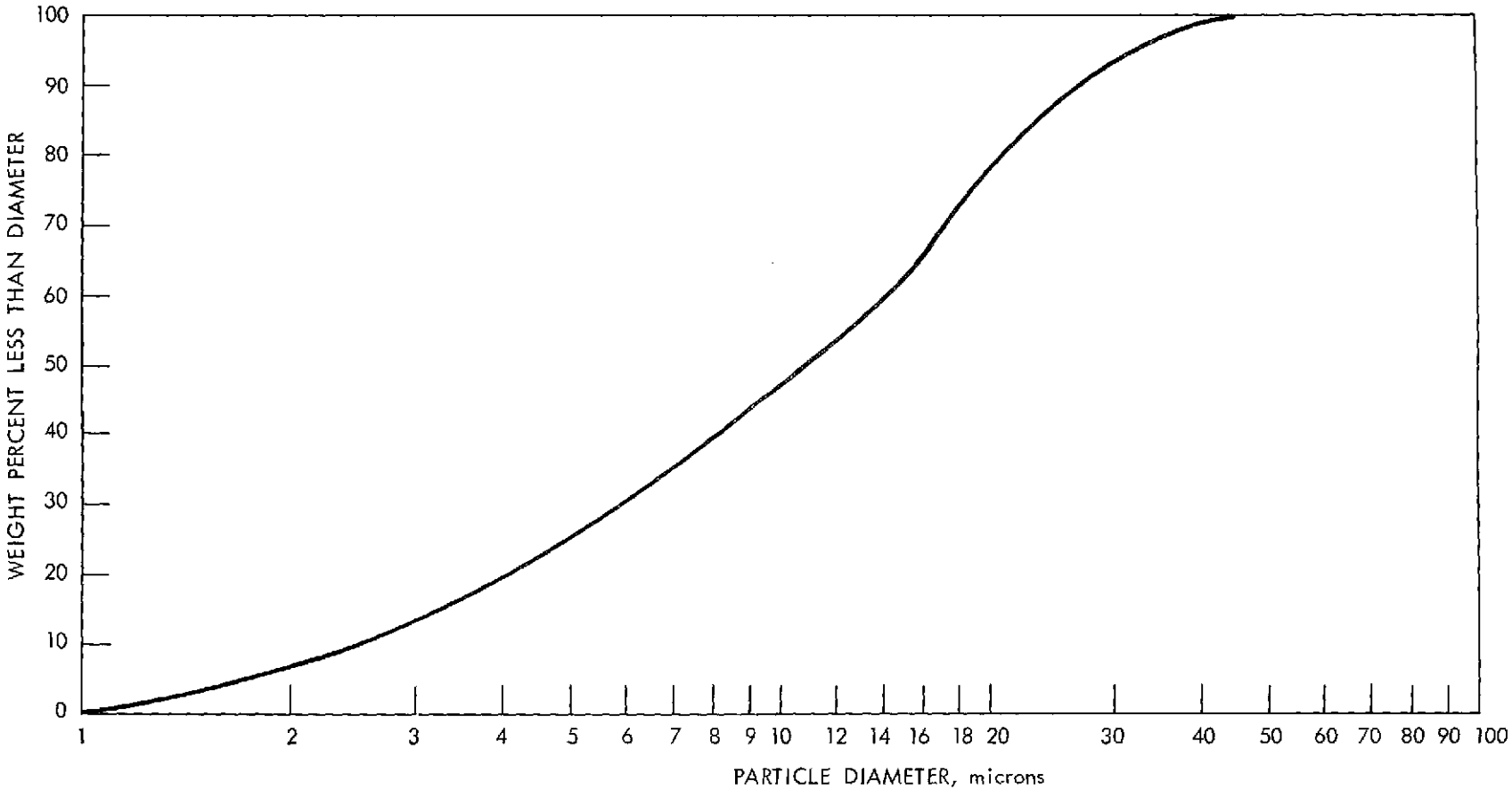
The generation of very small particles by vaporization-condensation takes place to some degree in the normal plasma jet process for uranium dioxide spheroidization. In each plasma jet spheroidization run, fines are generated and are collected on the reactor walls. In attempts to adjust operating conditions to maximize the production of this fine oxide, initial efforts resulted in conversion of about 50% of the starting material to fines. Only scoping studies have been conducted, but the smallest average particle size of the product has been 1.9 microns, while the largest average particle size has been 5 microns. A typical particle size distribution is presented in figure 5, and an electron



MICROMEROGRAPH PARTICLE SIZE DISTRIBUTION
OF URANIUM DIOXIDE GROUND IN A FLUID ENERGY MILL AND
SCREENED THROUGH 400-MESH STAINLESS STEEL SCREENS

Figure 2

DWG. NO. G-65-737



MICROMEROGRAPH PARTICLE SIZE DISTRIBUTION
OF URANIUM DIOXIDE GROUND BETWEEN ORBITING TUNGSTEN PLATES AND
SCREENED THROUGH 425-MESH PLASTIC SCREENS

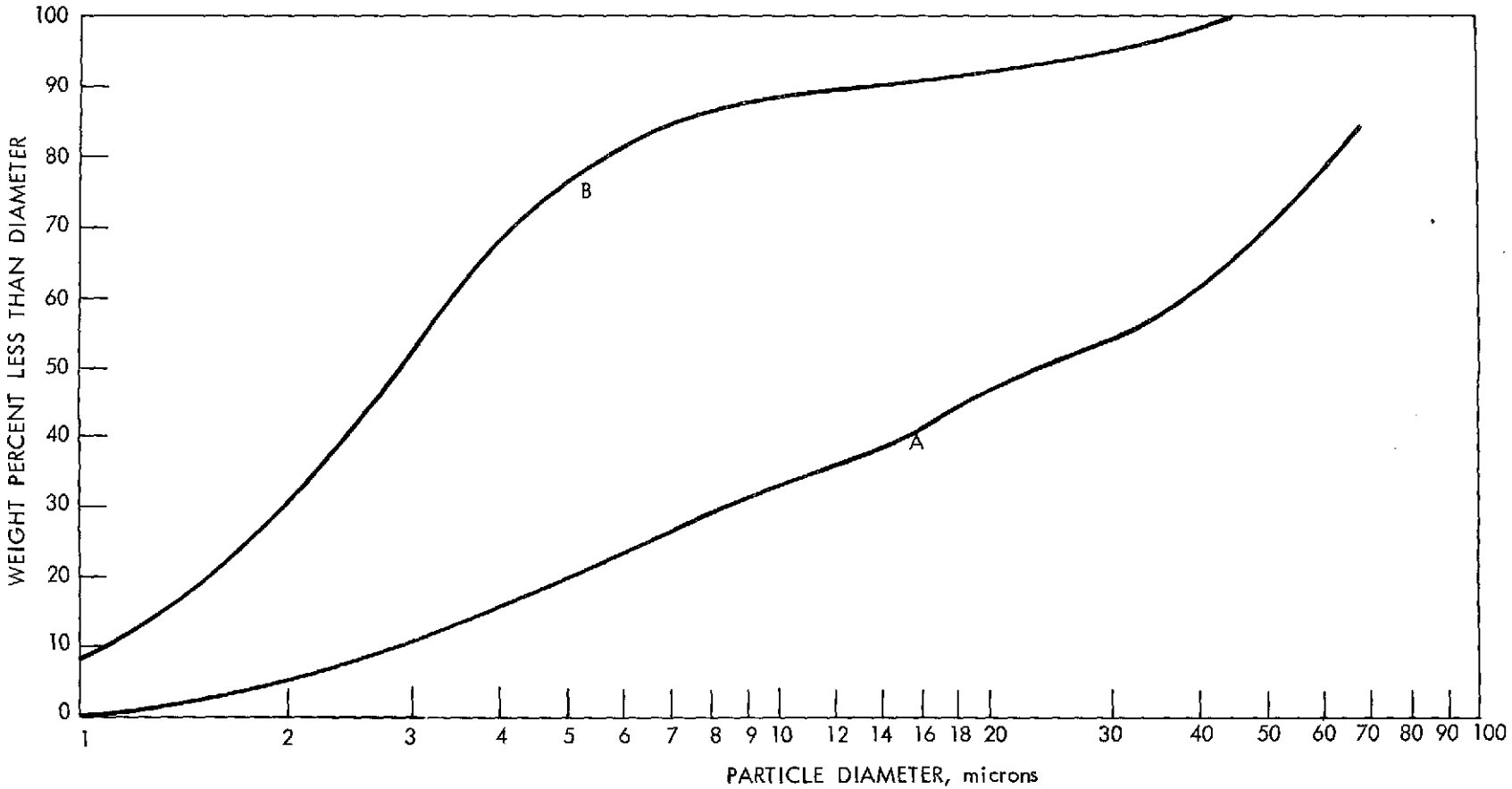
Figure 3

TABLE III

RESULTS OF URANIUM TRIOXIDE HYDRATION TESTS

Uranium Trioxide	Hydration Temp., °C.	Hydration Time, min.	Reduction Temp., °C.	Surface Area, sq.m./g.	Particle Size Distribution By Micromerograph, Diameter of Particles Below Indicated Percentage, microns			
					100%	75%	50%	25%
Hanford Continuous-Calciner	82	30	760	6.1	45.4	5.5	2.7	1.7
Weldon Spring Pot-Calcined	82	30	760	2.0	45.4	5.2	3.3	1.9
Hanford Continuous-Calciner	82	30	595	11.3				
Hanford Continuous-Calciner	82	15	595	4.2	54.5	18.2	5.3	1.8
Weldon Spring Fluid-Bed	82	30	760	3.3	45.4	5.1	2.9	1.8
Weldon Spring Pot-Calcined	82	30	760	3.5	54.5	3.6	2.7	1.9
Weldon Spring Fluid-Bed	As Received			1.3		55.5	24.4	6.9
New Weldon Spring Pot-Calcined	As Received			3.0		48.4	8.9	2.9

DWG. NO. G-65-738

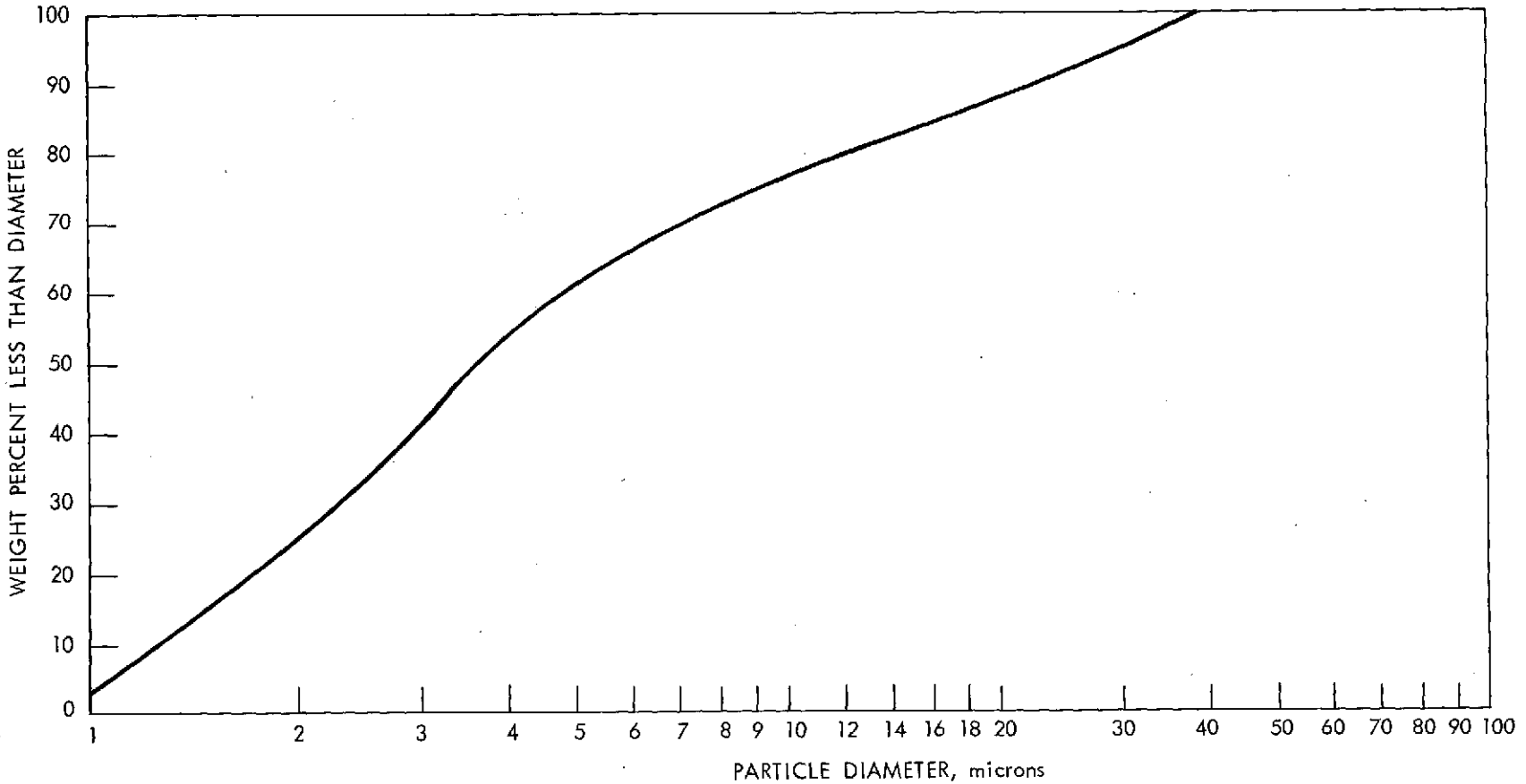


MICROMEROGRAPH PARTICLE SIZE DISTRIBUTION

A. As-Received Fluid-Bed Denitrated UO_3 (Bottom Curve)
B. Hydrated and Reduced Fluid-Bed Denitrated UO_3 (Top Curve)

Figure 4

DWG. NO. G-65-739



MICROMEROGRAPH PARTICLE SIZE DISTRIBUTION
URANIUM DIOXIDE POWDER PREPARED BY VAPORIZATION-CONDENSATION IN A PLASMA JET

Figure 5

micrograph is shown in figure 6.

Additional data have shown that the particle size of 1.9 microns measured by Micromerograph reflects the presence of agglomerates, since the material has a surface area of about 10 sq.m./g. and a crystallite size below 1 micron. Smaller particles have a tendency to collect on the upper portions of the reactor, while larger material is deposited lower down; thus, it may be possible, by appropriate collection techniques, to obtain several sized fractions from a single run.

All tests were made with uranium oxides. Experimental studies would be needed to determine if the vaporization-condensation technique is suitable for uranium dioxide containing additives, such as yttrium oxide. One of the major disadvantages of this technique is that many impurities are concentrated in the recondensed fraction; thus, stringent purity specifications would have to be set for the material fed to the jet. In addition, there is some evidence from X-ray diffraction analysis of the presence of free uranium metal in fine uranium dioxide prepared by the vaporization-condensation process in the reducing atmosphere of the plasma jet. This problem may be alleviated through the use of a neutral atmosphere. Further tests would be needed to establish the potentials of this method.

There are several problems associated with the production of a fine powder having a very sharp particle size distribution. Generally, the particle size distribution produced by the grinding operation is somewhat broad, unless some provision is made to separate the in-size particles as they are generated. Dry screening is not normally effective for classifying very small particles, since screens with a reasonable throughput rate are not available in this size range. While large-scale air classification systems exist, commercial air classification units are not available in the size needed to process 1-pound samples. Some progress has been made with liquid sedimentation techniques. A brief series of tests was run on gram quantities of powder to determine the technical feasibility of employing liquid sedimentation to separate 5- to 10-micron powder. The particles were ultrasonically dispersed in a liquid, and classification was achieved by sedimentation in gravitational or centrifugal fields. After predetermined settling periods, the desired fractions were removed, centrifuged, and vacuum-dried. These tests indicated that it is technically feasible to perform a sizing operation in this manner; however, some problems would have to be solved before an acceptable process could be developed. Water proved unsatisfactory as a settling medium because of the difficulty in producing a stable slurry. Technical grade isopropanol was a suitable liquid for the size separation; however, the product showed excessive carbon contamination. In addition, the vacuum-dried product was badly agglomerated. Finally, problems involved in scaling up the process to provide pound quantities of product require serious consideration.

In summary, while both the hydration-dehydration process and the vaporization-condensation process show promise for the preparation of fine particles of pure uranium dioxide, there would be complications in

Magnification - 60,000 X

URANIUM OXIDE PREPARED BY
VAPORIZATION-CONDENSATION IN A PLASMA JET

Figure 6

applying either of these techniques when the goal is a solid solution of uranium dioxide, plus one or more stabilizing agents. Preparation of the 1-pound sample of uranium dioxide containing 10 mole percent yttrium oxide in solid solution was accomplished in grinding and screening operations. The initial grinding was performed with orbiting tungsten plates, while the final grinding was done in a fluid energy mill. The particle size distributions of the powders at various stages in the size reduction operations appear in figure 7. Twenty passes through the fluid energy mill were required to obtain the desired size reduction to an average particle diameter of 2-1/2 microns.

Every reasonable effort was made to prevent impurity pickup during grinding. The surfaces of the equipment associated with the orbiting tungsten plates had been plasma sprayed with tungsten, and the interior of the fluid energy mill had been tungsten-coated either by plasma spraying or by vapor plating to avoid undesirable contaminants. Despite these precautions, some contamination occurred; however, as shown in table IV, the 1-pound sample of ultrafine uranium dioxide with 10% yttrium oxide in solid solution was within the purity specifications of 500 ppm. total detectable metallics. Thus, task 3 was completed with the preparation of this sample.

PROCESS FOR HIGH PURITY, ULTRAFINE URANIUM DIOXIDE (TASK 4)

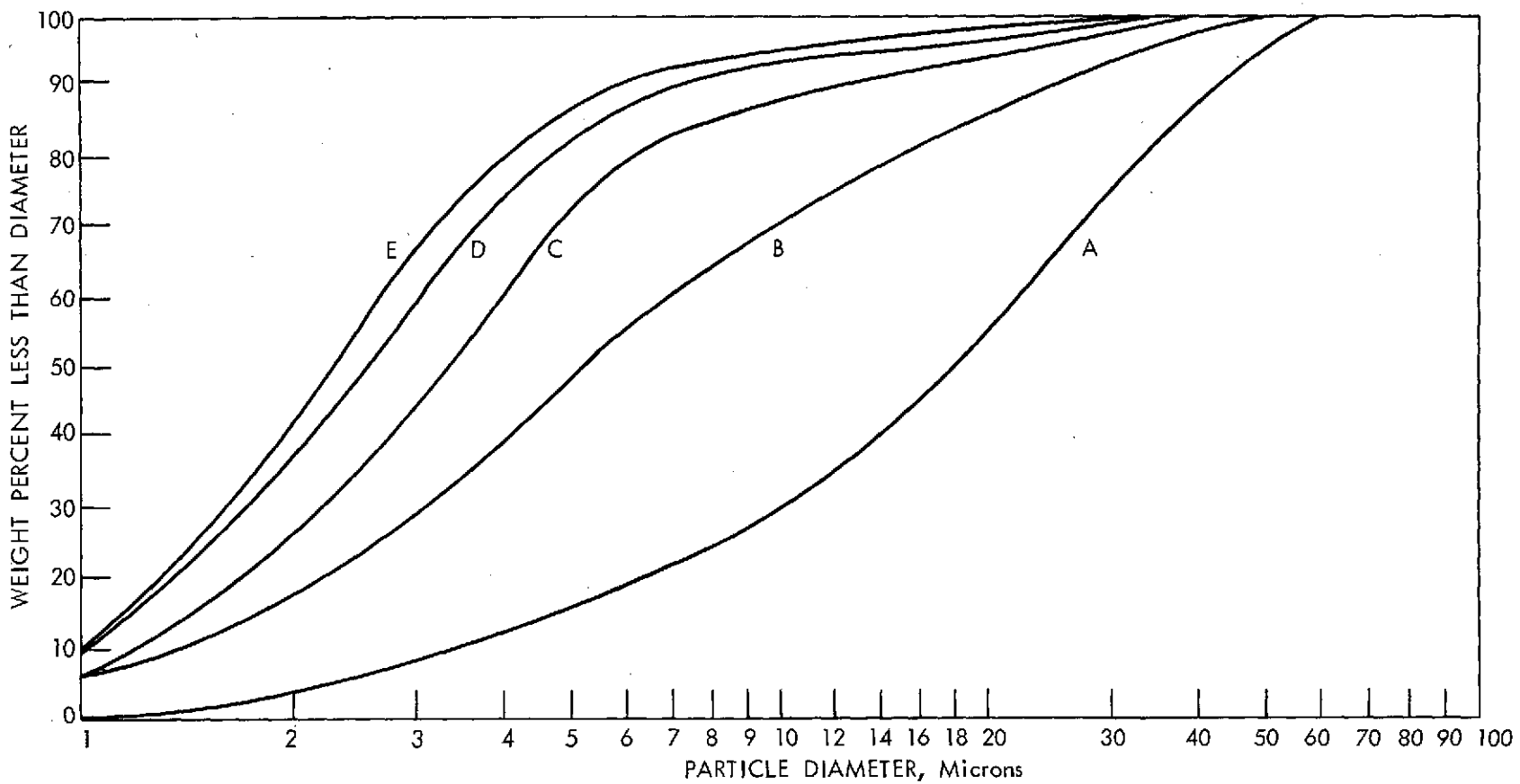
Since the objective of this task differed from that of task 3 only with respect to product purity, the work mentioned under task 3 was a logical step which had to be accomplished before this task could be undertaken. Recent grinding efforts are promising, but further technique development is required to prevent impurity pickup before the high purity, ultrafine, uranium dioxide can be produced.

SCALE-UP PRODUCTION OF MICRONIZED OR SPHEROIDIZED URANIUM DIOXIDE (TASK 5)

Previous studies at the ORGDP resulted in the development of techniques for producing high purity, spheroidal, stoichiometric uranium dioxide; and as noted under task 1, a 2-pound batch of this material in the 30- to 60-micron size range was prepared and was shipped to the NASA Lewis Research Center. The high cost of feed material, relatively low process efficiency, and low throughput rates resulted in a high product cost. During the first part of the fiscal year, efforts were directed toward process improvements which would reduce the unit cost of the spheroidized product.

Feed costs could be cut substantially by using urano-uranic oxide prepared in the manner employed on a commercial scale in AEC feed material plants. For experimental studies, a supply of uranium trioxide prepared by fluid-bed denitration was obtained from the AEC Weldon Spring Feed Material Center. Even though this oxide contained about 350 ppm. of detectable impurities, it was considered suitable for use in scale-up studies, since it should be possible to produce a high purity feed material by the fluid-bed denitration process at relatively low cost.

DWG. NO. G-65-540



Curve A: Ground between two orbiting tungsten plates.
Curve B:* Passed through fluid energy mill five times.
Curve C: Passed through fluid energy mill ten times.
Curve D: Passed through fluid energy mill fifteen times.
Curve E: Passed through fluid energy mill twenty times.

*Fluid energy mill operated at 40 psig. argon; all others passed through fluid energy mill at 80 psig. argon.

MICROMEROGRAPH PARTICLE SIZE DISTRIBUTION OF
URANIUM DIOXIDE-10 MOLE PERCENT YTTRIUM OXIDE
AT VARIOUS STEPS IN THE GRINDING PROCESS

Figure 7

TABLE IV

ANALYTICAL RESULTS FOR ULTRAFINE URANIUM DIOXIDE CONTAINING 10 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	$UO_2 + Y_2O_3$, Sintered and Ground: After Grinding Between Tungsten Plates To < 60 Microns	$UO_2 + Y_2O_3$, Sintered and Ground: Ground In Fluid Energy Mill, 15 Passes	$UO_2 + Y_2O_3$, Sintered and Ground: Ground In Fluid Energy Mill, 20 Passes*
Spectrochemical, ppm.				
Aluminum	10	2	5	5
Beryllium	-	3	3	3
Boron	-	-	1	1
Calcium	-	5	-	-
Chromium	25	5	120	120
Cobalt	1	-	-	-
Copper	2	2	10	25
Iron	150	-	200	200
Lead	-	-	-	3
Magnesium	1	60	60	60
Manganese	1	-	25	25
Nickel	5	2	35	-
Silicon	10	2	5	5
Sodium	-	3	15	20
Zinc	-	-	25	25
Total	205	84	504	492
Carbon, ppm.		30		
Tungsten, ppm.		900		
Uranium, %		79.8		
Yttrium, %		6.78		
O/U Ratio		2.14 ± 0.02		

* This is final product. Analysis made after passing powder through 325-mesh stainless steel sieve to remove agglomerates and stray coarse material.

Several plasma jet tests were made with the as-received uranium trioxide with generally poor results. This material is composed of rather frangible particles, and there was excessive particle breakup when it was passed through the plasma jet. Screening the uranium trioxide to minus 100, plus 325-mesh and then sintering the screened fraction in air at 1500°F. for 30 minutes to form urano-uranic oxide produced an acceptable feed that did not deagglomerate in the jet. The sintering operation is simple and inexpensive.

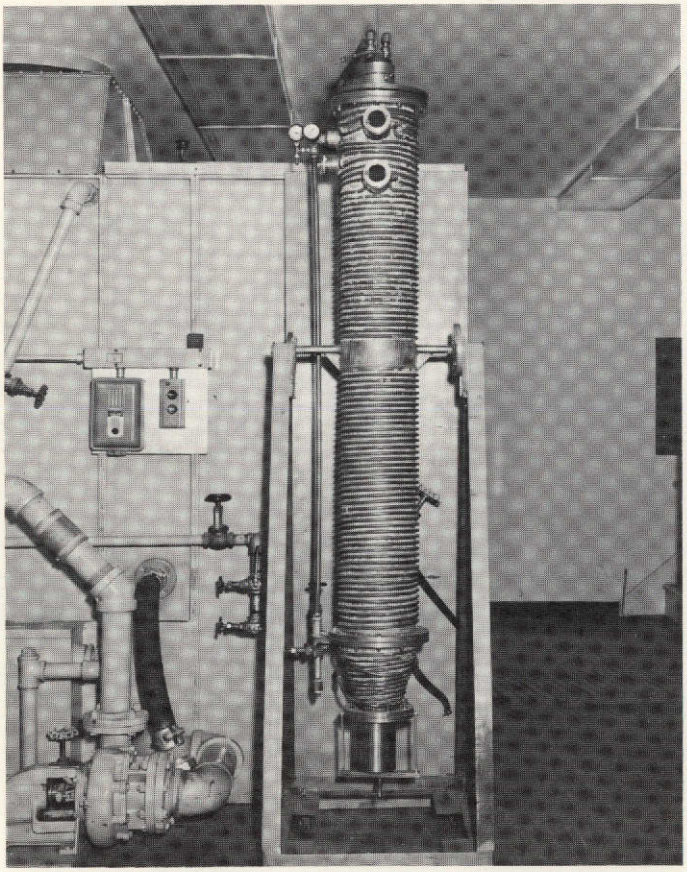
Sustained plasma jet throughput rates of up to 30 grams per minute were found to be practical. This rate was six times higher than the best achieved previously due primarily to the use of a higher energy helium plasma with the SG-1 plasma generator. In addition to the increased throughput possible with this system, a higher percentage spheroidization was achieved because of improved penetration of the feed particles into the high temperature plasma core. Electrode erosion occurred in the SG-1 plasma generator as it did in the M-4 generator used previously, but product contamination could be minimized by the use of tungsten-plated electrodes combined with frequent electrode inspection. The use of the higher energy system made it necessary to provide a longer particle quenching zone to prevent the particles from spattering on the collection area in the bottom of the reactor. A new reactor having a 2-foot longer quenching zone was fabricated for this work. A photograph of this 7-foot reactor appears in figure 8.

At least 2 pounds of contained in-size spheroids can now be produced daily. This represents a reduction in product cost of about an order of magnitude, as well as a significant increase in production capability. Because of a change in emphasis in the NASA program, this scale-up work was terminated prior to completion. Further efforts are required to control stoichiometry at the higher throughput rates if an oxygen-to-uranium ratio of 2.000 to 1 is necessary. In addition, further development of the upgrading system must be made to separate the spheroids from the nonspheroidal particles at the higher processing rates.

ADDITIONAL URANIUM DIOXIDE POWDERS (TASK 6)

A major effort has been placed on this task since a revision to the work statement in November, 1964, assigned it top priority. The revised program had two major objectives: (a) preparation of 1-pound batches of tungsten-coated, 30- to 60-micron uranium dioxide particles containing various oxide additives in solid solution; and (b) the preparation of 1-pound batches of these same materials as high purity, 1-micron size powders. After most of the first objective was completed, the program was again revised at the request of the NASA Lewis Project Manager to include the preparation of 1-pound batches of 30- to 60-micron uranium dioxide with six different concentrations of yttrium oxide in solid solution. The ultrafine powder production was then limited to the single batch of material containing 10 mole percent yttrium oxide discussed under task 3.

PHOTO NO. PH-65-428



NEW SPHEROIDIZATION REACTOR

Figure 8

a. Tungsten-Coated Uranium Dioxide Particles with Additives

This phase of the project required the preparation of a series of uranium dioxide powders with various oxide additives in solid solution. The powders were to be in the 30- to 60-micron size range, as equiaxed as possible, and near theoretical density and were to contain less than 300 ppm. total impurities when coated with 8 to 10 microns of tungsten[1,2]. Because of the high priority assigned this project, the impurity specification was relaxed when it appeared that the fluoride content of the coated powder could not be kept below 500 ppm. without further development of the vapor plating process. This assignment called for the preparation of pound lots of the following materials:

(1) Uranium dioxide without additives (control)

(2) Uranium dioxide containing 2-1/2 mole percent calcium oxide

(3) Uranium dioxide containing 5 mole percent calcium oxide

(4) Uranium dioxide containing 10 mole percent calcium oxide

(5) Uranium dioxide containing 5 mole percent yttrium oxide

(6) Uranium dioxide containing 5 mole percent thorium oxide

As the production of the above-mentioned material was being completed, the NASA Project Manager requested that the second phase of this project be limited to the production of pound samples of uranium dioxide containing various concentrations of yttrium oxide. Environmental tests conducted at NASA had indicated that the yttrium oxide was superior to either calcium oxide or thorium oxide as an additive for the prevention of uranium dioxide loss at elevated temperatures. The request was made for 1-pound lots of 30- to 60-micron uranium dioxide with yttrium oxide concentrations of 2-1/2, 5, 7-1/2, 10, 12-1/2, and 15 mole percent in solid solution, plus a control sample which had been processed by the same technique but which did not contain an additive. The procedures used to produce the uranium dioxide solid solution powders in the first phase of the project discussed immediately above were also to be used to prepare the powders with the various concentrations of yttrium oxide.

b. Ultrafine Uranium Dioxide with Additive in Solid Solution

The original request specified that powder with an average particle size of 1 micron be prepared. The revised work statement specified that the additives and concentrations were to be the same as for the initial series of 30- to 60-micron powders for a test of the effect of particle size on fuel element integrity. It was anticipated at that time that a substantial portion of these small powders would be generated as a by-product during the preparation of the 30- to 60-micron powder. As this work progressed, it became apparent that the

fine by-products would have relatively high impurity levels. Meanwhile, because of data generated at NASA, the production of the series of small powder was de-emphasized, and the Project Manager requested a sample of 5- to 10-micron powder which might possibly be suitable for vapor plating with tungsten in the fluidized bed. Before the 5- to 10-micron powder was produced, the objective was again revised. The final request was for the 1-pound sample of urania containing 10 mole percent yttria described under task 3.

General Procedures for Production of Solid Solution Powders

The preparation of the solutions involved the following operations: (a) powder blending and compaction, (b) compact sintering to form solid solution, (c) grinding the sintered pellets to the desired size powder. If required, the powder was then tungsten-coated by vapor plating. Workable techniques were established in each of the areas to the point that material could be produced on a regular basis, and samples have been prepared and shipped to NASA for evaluation. With the concurrence of the NASA Project Manager, work on sample preparation was started to meet a demanding schedule, even though some significant problems had not been solved; e.g., fluoride contamination of the oxide during vapor plating.

Powder Blending and Compaction

The initial tests were conducted with uranium dioxide made from pot-calcined uranium trioxide purchased from the AEC Weldon Spring Feed Material Center. Although this material was attractive from the standpoints of cost and purity level, it did not prove satisfactory as the starting material for the preparation of solid solutions by a diffusion process because of its relatively large particle diameter, 5 microns, and low surface area, 0.66 sq.m./g. More reactive, ceramic-grade uranium dioxide having a much higher surface area, 6 sq.m./g., and a smaller particle diameter, 3 microns, was purchased from the Y-12 Plant in Oak Ridge and was used in the preparation of all the uranium dioxide particles with and without additives mentioned previously.

The uranium dioxide, plus additive, was blended in a small tungsten rod mill for 1-1/4 hours prior to compaction. Due to rod mill size limitations, small batches of about 150 to 200 grams were first blended in the tungsten mill and then cross-blended by tumbling the batches together in a jar mill. Although there was no available measurement to determine accurately if adequate mixing had occurred, the mixtures produced this way had a uniform color, and discrete particles of additive could not be observed visually. Subsequent analysis of the solid solution powders by X-ray diffraction only showed the presence of a single phase, indicating adequate mixing had occurred.

Pellets, 3/4 inch in diameter and 3/8 inch thick, were formed in a double plunger die at compaction pressures of 75,000 psi. Compaction involved (a) loading the die with the bottom plunger in place, (b) inserting the top plunger and placing the assembly in the press, (c) pressing to 75,000 psi., (d) pressing the formed pellet from the die, and (e) cleaning

the die and plungers with a wire brush. Initial compactions made this way were slow, and 1 man could only turn out about 350 grams per day. Improvements, including a motor-driven pump for the press, increased the rate to about 1 kg. of pellets in a day per man. Further efforts to scale up the compaction process could not be justified on the basis of the current assignment; however, the transition from the present technique to one involving a tableting machine to pelletize large quantities of material should be straightforward.

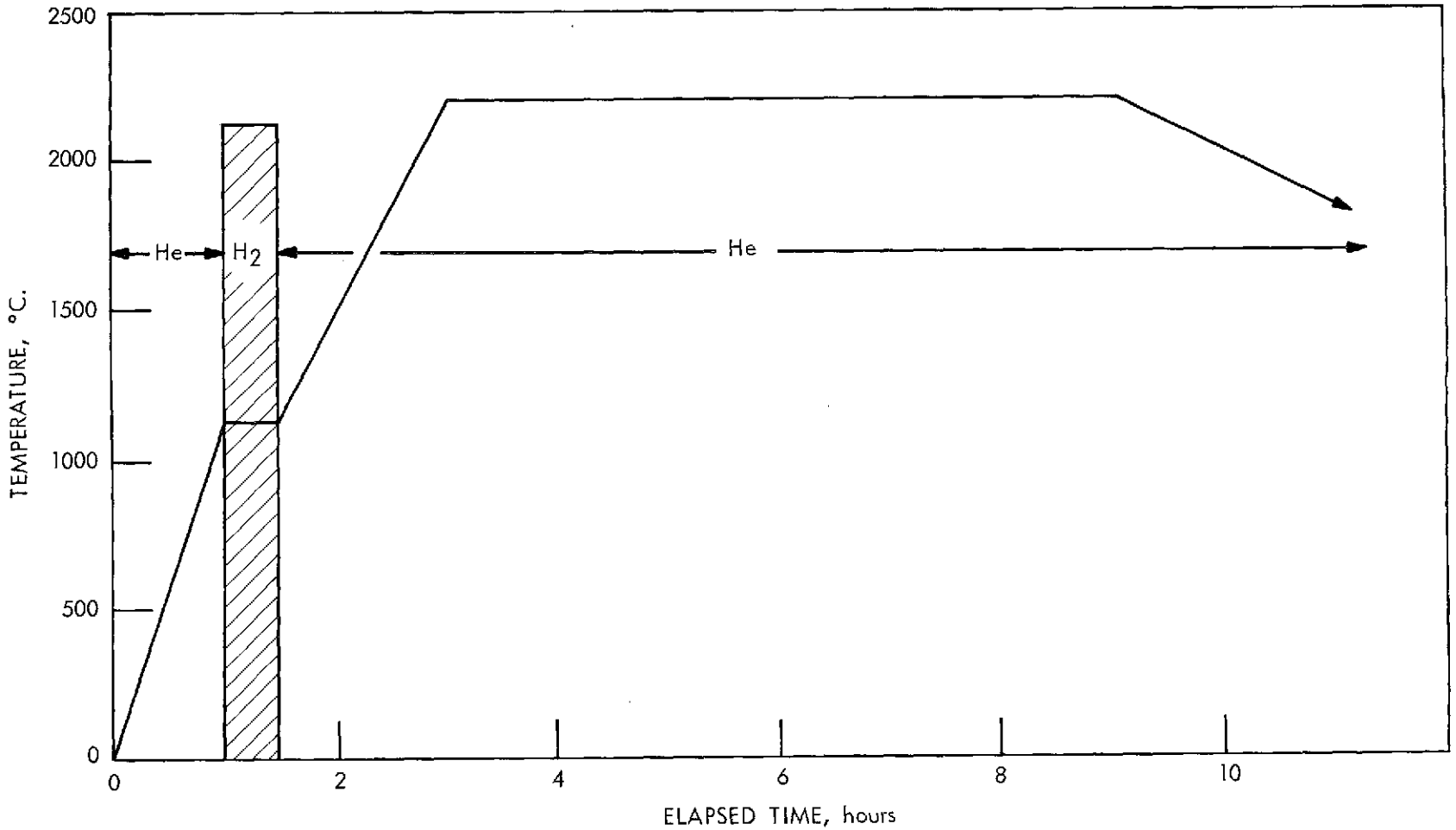
Pellets formed with the double plunger die were sturdy and generally held together well; however, the hygroscopic property of the calcium oxide resulted in considerable degradation of the pellets containing this additive. This degradation occurred during shipment of some of the unsintered pellets to NASA. Degradation did not occur when shorter times were involved between compaction and sintering.

Compact Sintering to Form Solid Solutions

The objective of the sintering operation was two-fold: (a) to reduce the ceramic-grade uranium dioxide which has an oxygen-to-uranium ratio of 2.32 to approximately stoichiometric composition, and (b) to hold the pellet at high enough temperatures for long enough times to form solid solutions by diffusion of the additive through the uranium dioxide matrix. As shown in figure 9, the furnace program involved a 1/2-hour treatment in hydrogen at 1100°C. to accomplish the reduction and a 6-hour treatment in helium at 2200°C. to form the solid solution.

The initial compact sintering was carried out at the ORGDP in an available graphite tube furnace. A total of four sintering runs was made. Two sintering runs were performed with the control uranium dioxide which had been rod milled and compacted as if it contained additive material, while the other two runs were made with uranium dioxide containing 2-1/2 mole percent calcium oxide. Because of high carbon contamination, plus the possibility of catastrophic furnace failure and resultant loss of valuable material, no further work was done in this furnace. It was then decided that the initial batches would be sintered at NASA, and the sintered material would be returned to ORGDP for further processing. A total of six batches of sintered pellets of ceramic-grade uranium dioxide with additives, weighing 550 grams each, was sintered at NASA during the early part of the program before facilities for sintering in-house became available. Sintering of the remaining batches was done at the Y-12 Plant, since several kilograms of pellets could be sintered at the same time, thereby lowering the cost of the sintering operation. One small batch of pellets was sintered in a resistance-heated furnace at ORGDP. The furnacing schedule, shown in figure 9, was met except for one run where treatment of a batch of uranium dioxide which did not contain additives was terminated at 1700°C. because of equipment failure. While this material was not suitable for control purposes, it was sintered sufficiently to be useful for tungsten coating tests. Following coating, it was shipped to NASA.

DWG. NO. G-65-740



SINTERING AND DIFFUSION CYCLE FOR THE PREPARATION OF OXIDE-URANIA SOLID SOLUTIONS

Figure 9

A tungsten muffle resistance furnace with a 10-inch long by 2-1/2-inch diameter hot zone has now been installed at the ORGDP. This furnace, shown in figure 10, is adequate for sintering 500-gram batches of material.

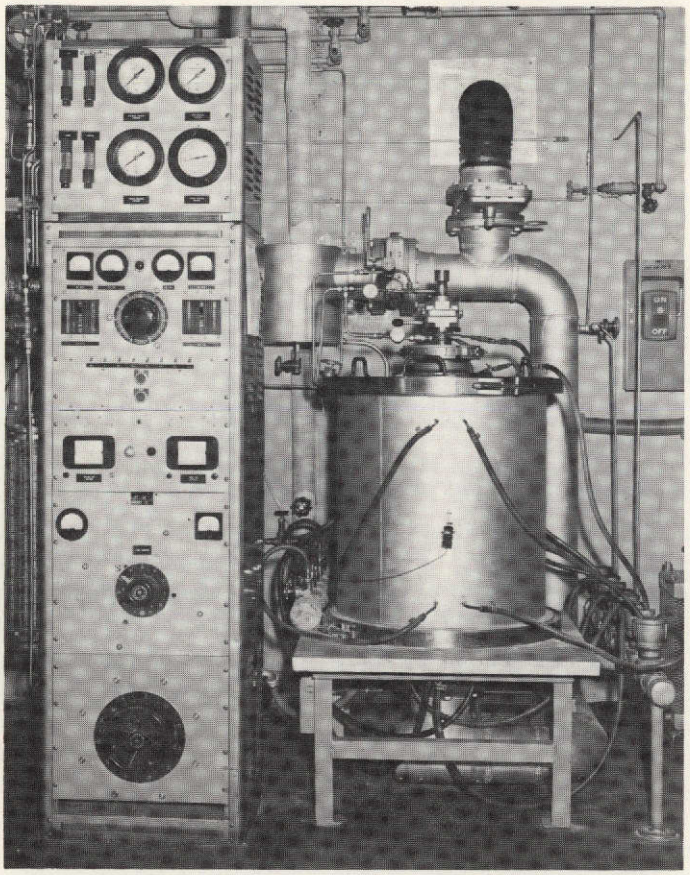
Grinding Sintered Pellets to Produce 30- to 60-Micron Powder

Three mechanical grinding techniques were investigated as methods of comminuting the sintered pellets to 30- to 60-micron powder. Included were (a) rod milling; (b) grinding in a mortar and pestle, followed by fluid energy milling; and (c) stamp milling between tungsten blocks, followed by grinding between two orbiting tungsten plates. The initial grinding studies were performed on uranium dioxide which had been sintered in the graphite tube furnace. This material was considered representative, since the pellets had been sintered to approximately the same physical condition as those formed at NASA and Y-12 in tungsten muffle furnaces. In these studies, no attempt was made to distinguish between pure uranium dioxide and uranium dioxide containing calcium oxide; however, further experience indicated that the difference in grindability between pure uranium dioxide and uranium dioxide containing the various additives did not exceed the batch-to-batch variability of pure uranium dioxide.

Rod Milling. A tungsten crucible about 6 inches long by 3 inches inside diameter with 5-inch long, 1/4-inch diameter tungsten grinding rods made a workable rod mill for grinding the uranium dioxide pellets. Sintered pellets were ground by contact with the inside of the vessel, the grinding rods, and each other. This action resulted in the formation of a large amount of smaller than 30-micron powder. The predominant grinding action appeared to be one of wearing away small particles from the pellets rather than gross crushing or fracturing of the pellets. In addition, the in-range, 30- to 60-micron powder was difficult to retrieve, since there was considerable tendency for the small particles to cling to the larger particles and also to agglomerate in the form of soft agglomerates. Even though Micromerograph analysis indicated that about 40% of the starting pellets ended up in the desired particle size range, the in-size powder was difficult to recover by screening; therefore, this approach was abandoned in favor of another.

Fluid Energy Milling. A tungsten carbide mortar and pestle was used initially to break up the pellets to minus 35-mesh to provide a suitable feed for the fluid energy mill. The initial fracturing also yielded some 30- to 60-micron powder, as well as fines, and the mortar and pestle could have been used to do all the grinding. This hand grinding was time consuming, however, and the final product was similar to that produced in the rod mill; i.e., difficult to screen if a high concentration of fines was permitted to build up. The fluid energy mill operates by impinging two powder-laden gas streams. Ideally, the entrained particles collide and fracture. At the conditions used for this study, some particle fracturing occurred; however, the milling action appeared to be primarily abrasive and resulted in the protrusions being knocked off the larger particles each time the powder was passed through the mill. The interior surfaces of the fluid energy mill used in this study had been coated with

PHOTO NO. PH-65-429



TUNGSTEN MUFFLE RESISTANCE FURNACE
Figure 10

tungsten by plasma spraying and vapor plating to avoid contamination of the product.

Some particles in the 30- to 60-micron range were generated on each pass, but these had to be removed before repassing through the mill or else the size was reduced further on subsequent passes. The use of the fluid energy mill, combined with repetitive screening, permitted about 40% of the starting material to be recovered in the 30- to 60-micron size range. The powder produced this way was clean and free-flowing, and many of the individual particles, though not truly spheroidal in shape, were quite equiaxed. Unfortunately, the processing rate was low, about 100 grams of in-size product per day, and the repeated screening was undesirable from a contamination standpoint. Further development of this process would be warranted only if higher production rates are needed.

Grinding Between Orbiting Tungsten Plates. In an effort to speed up the grinding operation and to improve product quality with respect to purity and yield, tests were conducted wherein grinding was done between two tungsten plates. It was reasoned that, if the powder were ground between two flat, parallel surfaces, the larger particles would receive the most grinding action. Development efforts led to a system which included a 3-inch wide strip of pure tungsten cemented in place in a tungsten coated, stainless steel tray. A second similar strip cemented to the base of an orbital sander acted against the fixed piece. Minus 30-mesh granules were produced by crushing the pellets between heavy blocks of tungsten, i.e., a manual version of a stamp mill, and this material was then ground to size between the stationary and orbiting plates. Yields were comparable to the fluid energy mill system, but the throughput rate was doubled.

Screening time was reduced, and only about one-half as many screening passes were needed to achieve the same yield. This system could be readily scaled up to handle larger quantities of materials without difficulty; however, a scale-up effort was not justified on the basis of the current assignment. Almost all of the 30- to 60-micron powder for NASA was ground by this technique.

Tests were made to compare the sieving efficiency and the degree of contamination from plastic screens with those of stainless steel screens. Generally, more efficient screening was possible with stainless steel screens. No metallic impurity resulted from the plastic screens, but there was more possibility for the contaminant, carbon, to be eroded from the screens and to get into the product. Analytical results failed to show a significant decrease in impurities through the use of the plastic screens, so stainless steel screens were used for the remainder of the screening.

Particle Coating by Hydrogen Reduction of Tungsten Hexafluoride in a Fluidized Bed

Techniques have been developed and procedures have been established to deposit a layer of tungsten onto uranium dioxide powder by the hydrogen reduction of tungsten hexafluoride in a fluidized bed. Tungsten

hexafluoride is reduced to tungsten metal in the presence of hydrogen at temperatures above 455°C. This reaction takes place on any heated surface, and prolonged operation results in the formation of a progressively thicker layer of tungsten metal. Unfortunately, the reduction reaction liberates hydrogen fluoride which reacts with uranium dioxide to form uranium fluorides deemed undesirable in the final product. The problem of coating can be divided into two rather broad categories; namely, (a) the mechanical operation of the fluid bed, and (b) the chemistry associated with fluoride contamination.

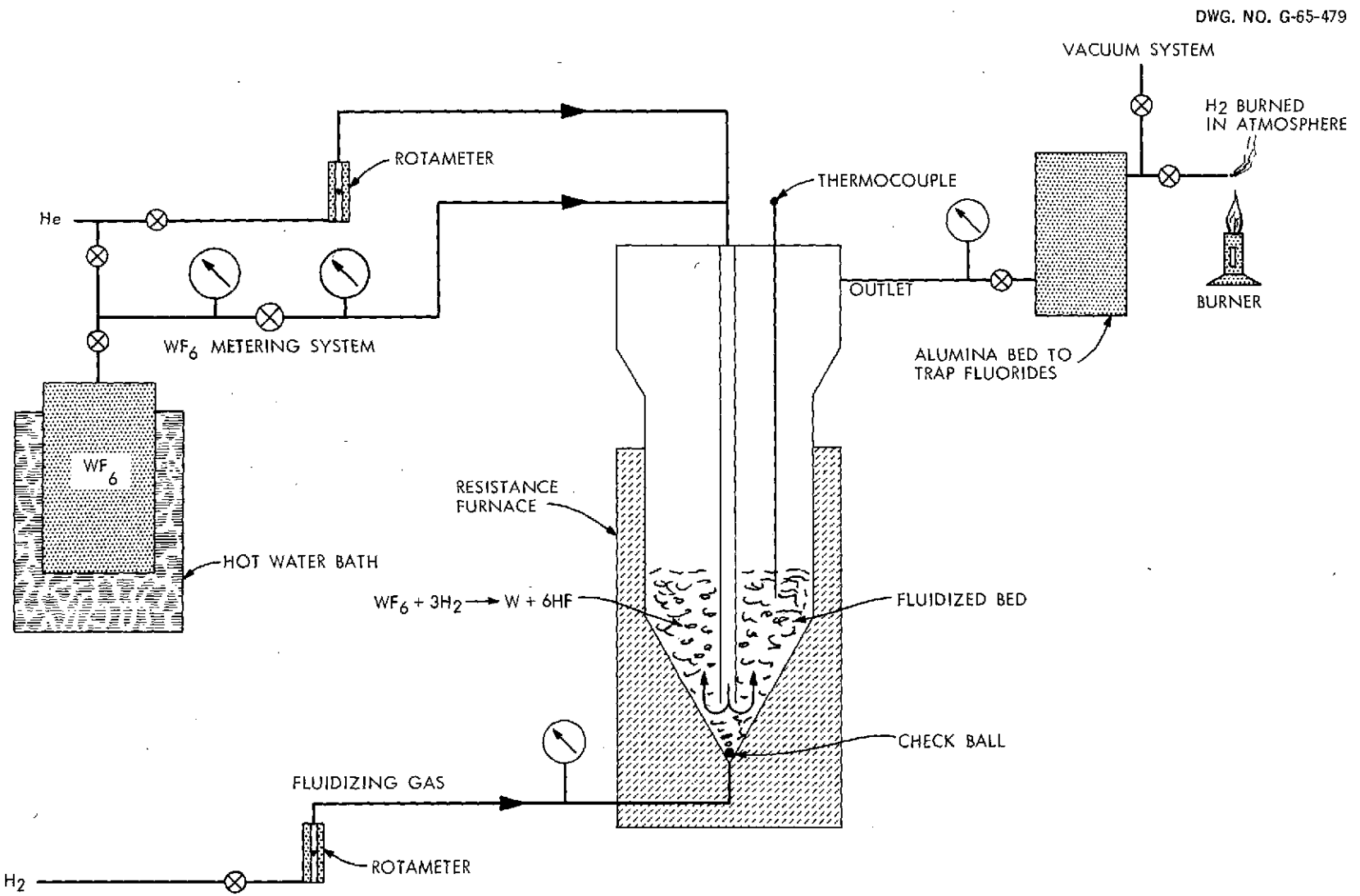
A flow diagram of the coating system used for tungsten plating the uranium dioxide powders is shown in figure 11. Hydrogen, used as the fluidizing gas, as well as a primary reactant, was purified*, metered, and fed to the bed through a ball check in the conical bottom of the vertically mounted, cylindrical reactor. The tungsten hexafluoride was vaporized, metered through calibrated capillaries, and injected into the bed through a line extending from the top of the reactor. To prevent powder accumulation or hydrogen backflow through this line, a helium bleed was maintained. This helium flow also increased the velocity of the tungsten hexafluoride stream and decreased the tungsten hexafluoride concentration, thus preventing excessive plating at the top of the feed line. The off-gases passed through an entrainment separator at the top of the reactor, through alumina traps to remove hydrogen fluoride and were then burned and exhausted through a fume hood. Bed temperature was measured with an internal thermocouple and was controlled by manually adjusting a variac supplying power to the resistance heater surrounding the lower part of the reactor. Inlet and outlet reactor pressures were used to indicate fluidization, as well as bed or line plugging.

Using 30- to 60-micron uranium dioxide, the powder action more nearly resembled a slugging bed than that usually associated with a classical fluidized bed. Such bed action is not unexpected considering the density and particle size and distribution of the powder to be fluidized. Another problem arose from the increase of both particle size and particle density during the coating run. Fluidization could be maintained by increasing the hydrogen flow; however, this resulted in varying hydrogen-tungsten hexafluoride ratios, since known incremental changes in the tungsten hexafluoride feed rates were difficult to make.

In spite of these problems, very little trouble with bed caking, powder agglomeration, or uneven coating was experienced during production coating runs. In the early development runs, considerable bed and outlet gas line plugging occurred, but this was eliminated by installing an efficient hydrogen purification system. The evidence is that the action taken to purify the hydrogen eliminated formation of less volatile oxyfluorides. In various experimental coating runs, especially those made at temperatures above 700°C. or with very high tungsten hexafluoride feed rates, some bed caking resulted from the rapid reaction rate. At these high

---

* The hydrogen was passed through a bed of heated copper wool to remove oxygen and through Molecular Sieves to remove water.



FLOW DIAGRAM OF FLUID BED TUNGSTEN COATING SYSTEM

Figure 11

tungsten hexafluoride feed rates, there was also uranium dioxide loss by elutriation.

Fluid-bed runs are summarized in table V. Generally, it was advantageous to make two or more coating runs with each batch of powder to allow inspection and sampling for control of plate thickness and also to transfer the powder to a large reactor as the bed weight increased. The intermediate shutdown point was determined largely by the quantity of material contained in the starting bed. The hydrogen flow rates shown in the table are average values for about the middle of the coating run, while the tungsten hexafluoride rates were average values calculated at the end of the run from a change in the weight of the tungsten hexafluoride feed cylinder.

The back reaction of the liberated hydrogen fluoride with the uranium dioxide in the bed produced fluoride compounds unwanted in the final powder. Efforts to decrease the fluoride content in the coated powder by adjustment of bed temperature and reagent concentrations were only partially effective. Development of a plating procedure which would result in low fluoride content of the coated powder was hampered by the lack of powder for test purposes. Such powder was not readily available, since the same effort was required to produce test powder as to prepare the actual powder for coating. The picture is made more complex by the presence of the additives in the powder to be coated as there is some indication that the additives, particularly calcium oxide, contribute to the high fluoride content. The highest fluoride contents are found in the powders containing calcium oxide. It is therefore conceivable that different coating conditions may be needed to obtain low fluoride content for powders containing additives. To meet schedules, plating conditions were frozen before a completely satisfactory solution had been obtained to the fluoride problem.

Preparation of the First Series of NASA Samples

To meet the first objective in this task, the following batches of tungsten-coated uranium dioxide were prepared and were shipped to NASA:

a. Uranium dioxide without additives (control)

b. Uranium dioxide containing 2-1/2 mole percent calcium oxide

c. Uranium dioxide containing 5 mole percent calcium oxide

d. Uranium dioxide containing 10 mole percent calcium oxide

e. Uranium dioxide containing 5 mole percent yttrium oxide

f. Uranium dioxide containing 5 mole percent thorium oxide

Each batch contained approximately 1 pound of uranium dioxide.

TABLE V

FLUID-BED OPERATING CONDITIONS AND FLUORIDE CONTENTS OF TUNGSTEN-COATED POWDER

Run Number	Bed Material	Run Time, hr.	Plate Thickness, microns	Feed Rate*		Bed Weight, grams		Final Fluoride Content, ppm.
				WF_6 cc./min.	H_2, cfh.	Starting	Ending	
WF-246	30- to 60-Micron UO_2 Without Additives	1/3†	< 1‡	150	8	180	170	5,200
WF-248		3-1/4	5.1	150	9	163	365	780
WF-249		2-1/2	7.9	175	14	335	500	520
WF-250	30- to 60-Micron UO_2 Containing 5 m/o Y_2O_3	4	6.8	275	8	184	568	1,200
WF-251		1-2/3	8.5	225	14	514	651	980
WF-247	44- to 53-Micron Pure Tungsten Powder	2	1.5	150	14	307	414	< 20
WF-252	30- to 60-Micron UO_2 Containing 2.5 m/o CaO	1-3/4	4.5‡	406	5	224	511	2,300
WF-253		3	10.0	367	10	494	913	980
WF-254	30- to 60-Micron UO_2 Containing 5 m/o CaO	2	4‡	354	5	215	497	3,500
WF-255		2-3/4	10.3	388	6	489	882	1,900
WF-256	Control, 30- to 60-Micron UO_2 Without Additives	1-2/3	2‡	384	7	520	740	4,400
WF-257		2-5/6	4.5‡	464	8	714	1,255	2,000
WF-258		3-1/2	10.5	670	8	1,245	2,094	980

TABLE V (Contd.)

FLUID-BED OPERATING CONDITIONS AND FLUORIDE CONTENTS OF TUNGSTEN-COATED POWDER

Run Number	Bed Material	Run Time, hr.	Plate Thickness, microns	Feed Rate*		Bed Weight, grams		Final Fluoride Content, ppm.
				WF_6, cc./min.	H_2, cfh.	Starting	Ending	
WF-261	30- to 60-Micron UO_2	1-2/3	-	406	4.5	220	486	8,100
WF-262	Containing 10 m/o CaO	2-3/4	8.1	375	5.0	470	897	3,900
WF-268	30- to 60-Micron UO_2 Containing 5 m/o CaO	1-1/2	-	519	6.0	330	626	6,400
WF-269		2	-	549	6.5	595	1,040	4,000
WF-270		1	7.6	560	7.0	1,030	1,220	1,100
WF-267	30- to 60-Micron UO_2	2-3/4	-	569	7.0	712	1,262	2,000
WF-271	Containing 2.5 m/o CaO	1/2	8.1	640	8.0	1,238	1,342	1,900
WF-272	30- to 60-Micron UO_2	1-1/2	-	540	6.5	270	531	9,400
WF-274	Containing 10 m/o CaO	3-2/3	9.4	516	8.0	523	1,184	5,900
WF-275	30- to 60-Micron UO_2	1-7/12	3.0	472	5.0	346	660	2,200
WF-276	Containing 5 m/o Y_2O_3	3-1/3	8.8	365	8.5	636	1,472	1,300
WF-277	30- to 60-Micron UO_2	1-1/2	-	492	5.5	500	803	3,000
WF-278	Containing 5 m/o ThO_2	3-1/2	7.7	670	6.5	785	1,791	1,320

TABLE V (Contd.)

FLUID-BED OPERATING CONDITIONS AND FLUORIDE CONTENTS OF TUNGSTEN-COATED POWDER

* Approximately 1 cfh. of helium was fed with the tungsten hexafluoride in all runs.
  a. Hydrogen flow rate varied from the average by ± 15% as required to maintain fluidization.
  b. Tungsten hexafluoride rates probably varied within ± 10% of the average during the run.

† Run terminated prematurely when outlet line plugged.

‡ Estimated from weight change.

Note: Plating temperature for all runs was 565 to 595°C.
  a. Except for WF-247, all initial plating runs were reduced at 870°C. for 4 hours prior to plating. Run WF-247 was reduced for 1 hour at 650°C.
  b. All secondary runs were reduced at 815 to 870°C. for 1 hour prior to plating.

Photomicrographs of six different sectioned samples of coated powder are shown in figures 12, 13, 14, 15, 16, and 17. In each case, uniform, crack-free coatings are apparent. No explanation can be offered to account for the voids present in some of the particles, while no voids are apparent in others even though all the powders received essentially the same treatment.

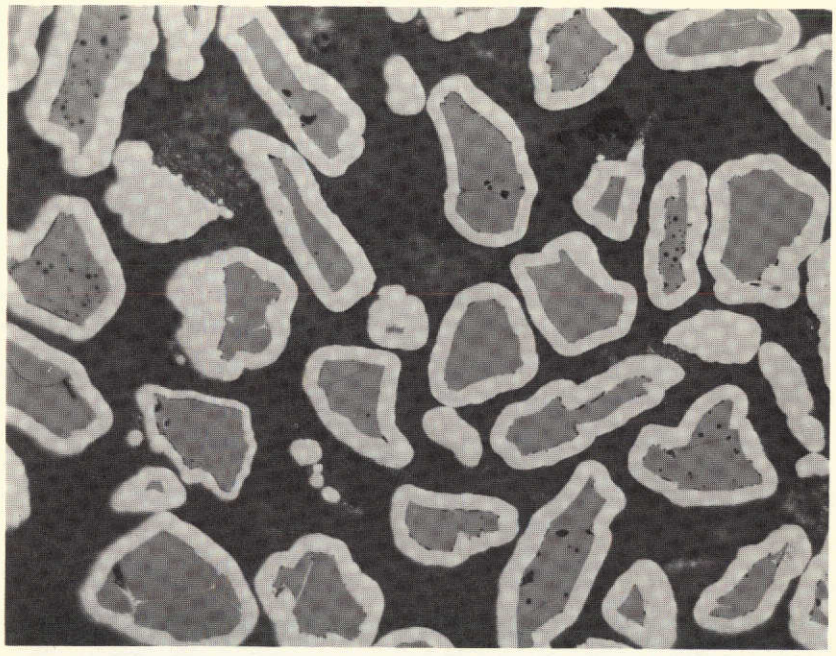
Analytical results for the various powders are shown in tables VI through XVI. Limits of detection for spectrochemical analyses on uranium dioxide and coated uranium dioxide are presented in tables II and XVII, respectively. Based on spectrochemical analyses, total metallic impurities in the tungsten-coated products were in the 20 to 40 ppm. range. With regard to these analyses, it should be noted that the results of the spectrochemical analyses were obtained using pure uranium dioxide standards. A single set of tests indicated that yttrium oxide and thorium oxide additives did not affect the spectrochemical results; however, calcium oxide additive suppressed all impurities; i.e., gave lower values. The impurity level in the final coated product was surprisingly low, based either on the impurities in the ceramic-grade uranium dioxide used as starting material or on the impurities in the ground and screened intermediates. Data from subsequent studies indicate that particulate impurities may have been elutriated from the fluid bed during reduction, i.e., before tungsten coating, and that this may account for the low impurity level in the final product.

The oxygen-to-uranium ratios indicated that, generally, the powders were slightly substoichiometric; however, this interpretation is open to question because of the undetermined effects of tungsten contaminants and the stoichiometry of the oxide additive on the analytical results. Chemical analyses for additive concentrations generally agreed well with values calculated from the amount of oxide added to the uranium dioxide. X-ray diffraction analyses indicated the additives are present as solid solutions. A comparison of the additive concentrations determined by different means is presented in table XVIII*, and the change in lattice constant due to the various additives is shown in figure 18*.

The value of 5.4763 A. by X-ray diffraction for the cell edge length of the thoriated material is in excellent agreement with theoretical values. The theoretical and measured values obtained for the calcium oxide additive series show excellent agreement at the highest concentration; however, the agreement is poor at the lower concentrations. Theoretical data were not available to predict the cell edge length that would be expected with the yttrium oxide additive; however, it can be seen that a fairly linear relationship was obtained over the range of yttrium oxide concentration examined.

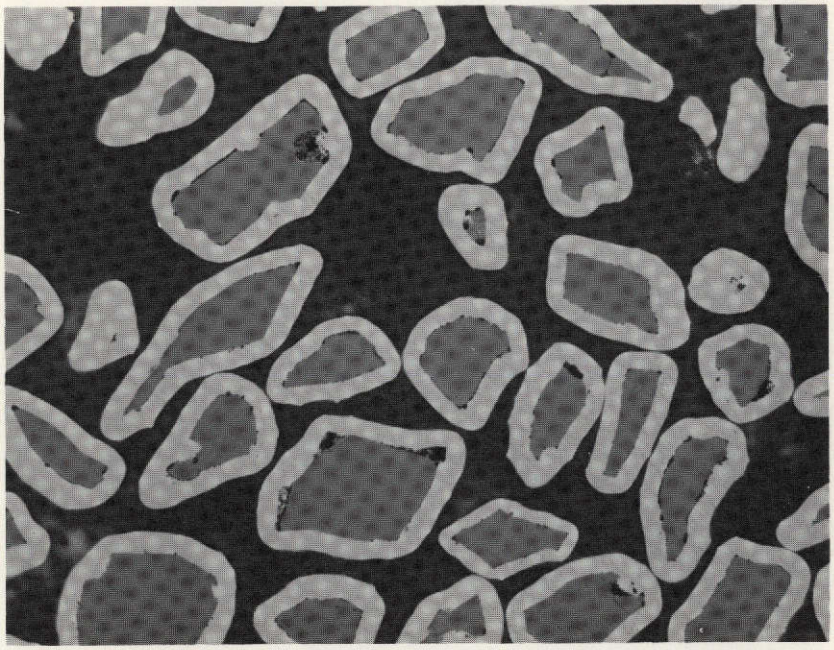
---

* Results for the second series of powders containing various concentrations of yttrium oxide are included.



WF-249 Magnification - 250X

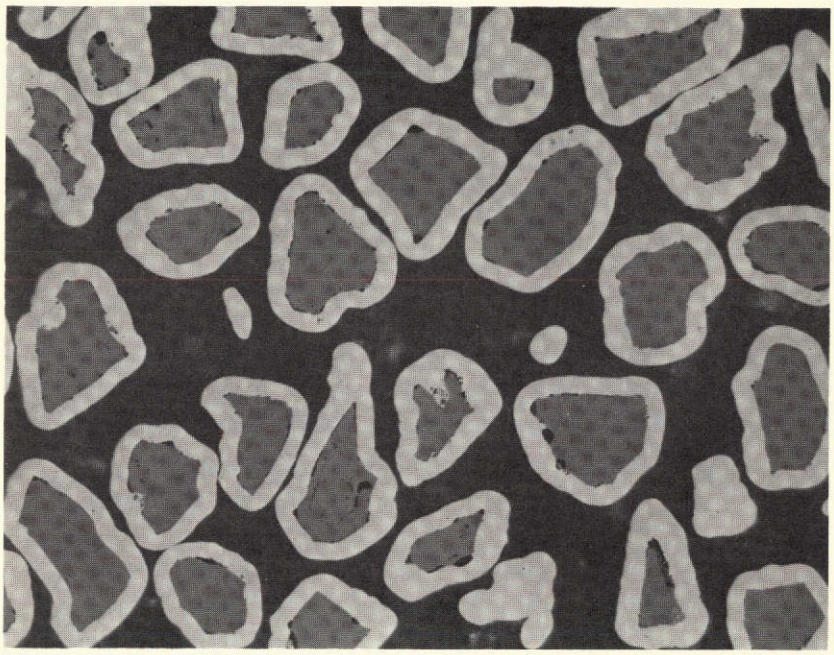
UO_2 POWDER WITHOUT ADDITIVES
COATED WITH 7.9 MICRONS OF TUNGSTEN
(CrO_3 Attack Polish)
Figure 12



WF-253 Magnification - 250X

UO_2 POWDER WITH 2.5 m/o CALCIUM OXIDE ADDITIVE
COATED WITH 10.0 MICRONS OF TUNGSTEN
(CrO_3 Attack Polish)

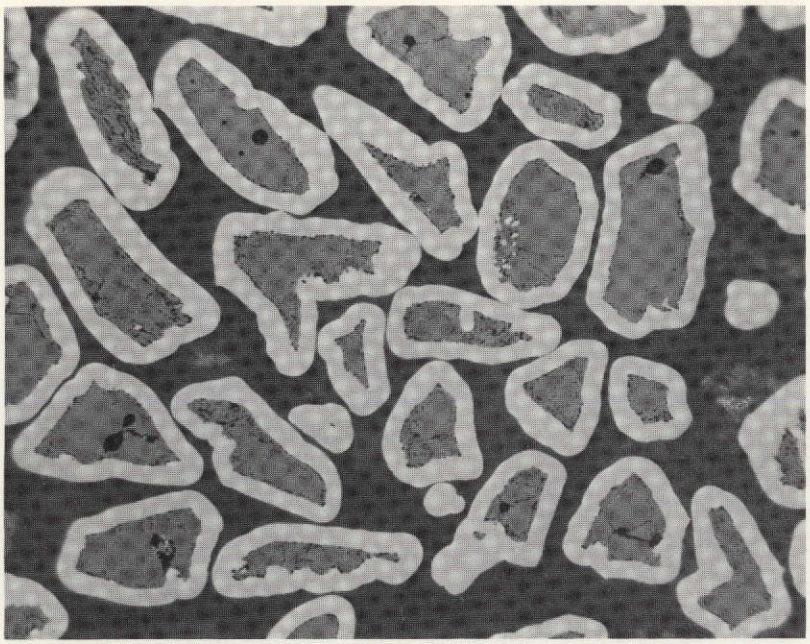
Figure 13



WF-255 Magnification - 250X

UO_2 POWDER WITH 5 m/o CALCIUM OXIDE ADDITIVE
COATED WITH 10.3 MICRONS OF TUNGSTEN
(CrO_3 Attack Polish)

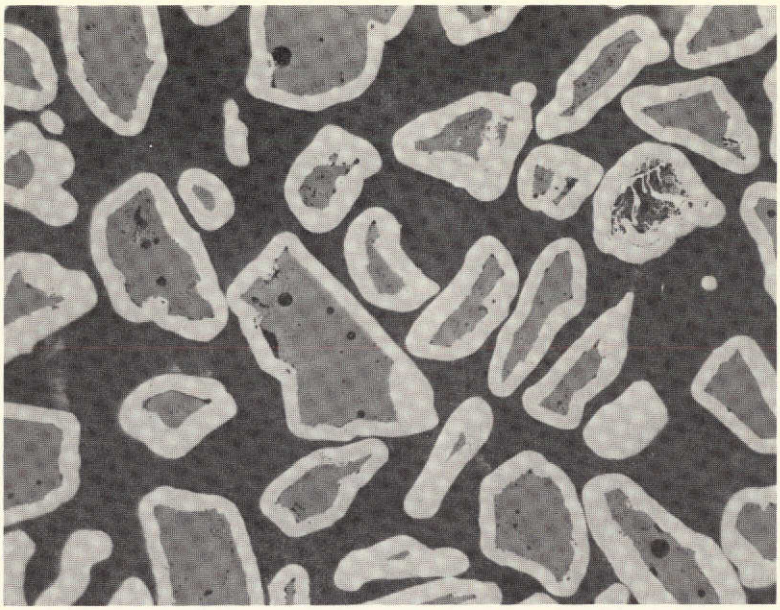
Figure 14



WF-274 Magnification - 250 X

UO_2 POWDER WITH 10 m/o CALCIUM OXIDE ADDITIVE COATED WITH 9.4 MICRONS OF TUNGSTEN (CrO_3 Attack Polish)

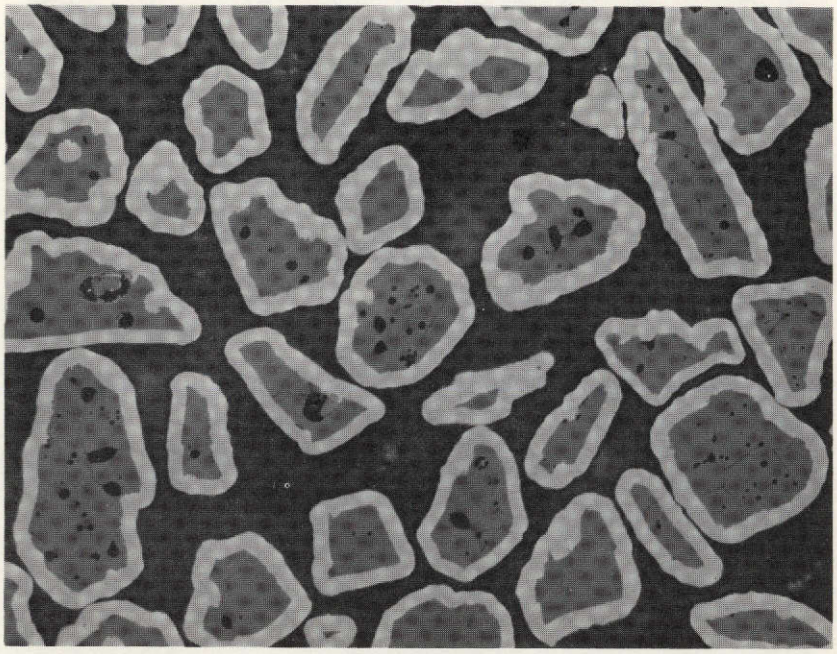
Figure 15



WF-278 Magnification - 250 X

UO_2 POWDER WITH 5 m/o THORIUM OXIDE ADDITIVE
COATED WITH 7.7 MICRONS OF TUNGSTEN
(CrO_3 Attack Polish)

Figure 16



WF-251 Magnification - 250X

UO_2 POWDER WITH 5 m/o YTTRIUM OXIDE ADDITIVE
COATED WITH 8.5 MICRONS OF TUNGSTEN
(CrO_3 Attack Polish)

Figure 17

TABLE VI

ANALYTICAL RESULTS FOR URANIUM DIOXIDE SINTERED FOR 1 HOUR AT 1700°C. IN A RESISTANCE-HEATED FURNACE

Element	Ceramic-Grade UO_2 Purchased from Y-12	UO_2 Sintered, Ground, and Sized		
		> 500-Micron	30- to 60-Micron	30- to 60-Micron with a 7.9-Micron Tungsten Coating, WF-249
Spectrochemical*, ppm.				
Aluminum	10	35	35	1
Cadmium	-	1	1	-
Calcium	-	-	-	5
Chromium	25	35	35	10
Cobalt	1	-	-	-
Copper	2	2	5	1
Iron	150	200	200	10
Lead	-	-	5	-
Magnesium	1	35	25	-
Manganese	1	2	2	-
Nickel	5	5	10	10
Silicon	10	150	120	1
Tin	-	-	1	-
Total	205	465	439	38
Tungsten, %				74.6
Uranium, %	86.53	88.24	88.27	20.7
O/U Ratio	2.32	1.98	1.98	
Fluoride, ppm.				520

* Listings of elements sought by spectrochemical analysis, together with the limit of detection, are presented in tables II and XVII.

TABLE VII

ANALYTICAL RESULTS FOR
URANIUM DIOXIDE CONTROL CONTAINING NO ADDITIVE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing No Additive, Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	30- to 60-Micron With a 10.5-Micron Tungsten Coating, WF-258
Spectrochemical, ppm.*				
Aluminum	10	60	120	-
Calcium	-	25	25	-
Chromium	25	60	35	5
Cobalt	1	3	3	-
Copper	2	25	2	-
Iron	150	150	120	5
Magnesium	1	25	35	1
Manganese	1	5	2	-
Molybdenum	-			18
Nickel	5	25	5	10
Silicon	10	5	5	1
Sodium	-	3	1	-
Tin	-	1	-	-
Titanium	-	-	-	7
Vanadium	-			3
Total	205	387	353	50
Carbon, ppm.		89	34	4
Fluoride, ppm.				980
Uranium, %	86.53	88.22	88.26	17.0
Tungsten, %				78.7
O/U Ratio	2.32	1.99	1.98	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in tables II and XVII.

TABLE VIII

ANALYTICAL RESULTS FOR URANIUM DIOXIDE CONTAINING 2.5 MOLE PERCENT CALCIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased from Y-12	UO_2 Containing 2.5 m/o CaO Sintered at NASA, Ground, and Sized	
		< 30-Micron	30- to 60-Micron With a 10-Micron Tungsten Coating, WF-253
Spectrochemical*, ppm.			
Aluminum	10	25	-
Chromium	25	150	10
Cobalt	1	-	-
Copper	2	35	-
Iron	150	300	10
Lead	-	5	-
Magnesium	1	300	1
Manganese	1	10	-
Nickel	5	25	5
Silicon	10	4	1
Sodium	-	5	-
Tin	-	2	-
Zinc	-	35	-
Total	205	896	27
Tungsten, %			77.1
Uranium, %	86.53		18.5
O/U Ratio	2.32		
Fluoride, ppm.			980
Carbon, ppm.		94	6
Calcium, %		0.59	

* Listings of elements sought by spectrochemical analysis, together with the limit of detection, are presented in tables II and XVII.

TABLE IX

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 2.5 MOLE PERCENT CALCIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 2.5 m/o CaO Sintered at Y-12, Ground, and Sized			
		Pellets	< 30-Micron	30- to 60-Micron	30- to 60-Micron With an 8.1-Micron Tungsten Coating, WF-271
Spectrochemical, ppm.*					
Aluminum	10	25	10	10	-
Chromium	25	5	35	35	10
Cobalt	1	-	-	-	
Copper	2	1	10	2	1
Iron	150	10	120	60	10
Lead		-	5	-	-
Magnesium	1	60	120	25	-
Manganese	1	1	2	1	-
Nickel	5	5	5	5	10
Silicon	10	2	1	1	-
Silver	-	-	-	-	1
Tin	-	-	5	1	-
Total	205	109	313	140	32
Carbon, ppm.			15	7	18
Calcium, %			0.33	0.37	0.08
Fluoride, ppm.					1,900
Tungsten, %			0.08	0.07	74.8
Uranium, %	86.53		87.68	87.63	20.8
O/U Ratio	2.32		2.00	2.00	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in tables II and XVII.

TABLE X

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 5 MOLE PERCENT CALCIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 5 m/o CaO Sintered at Y-12, Ground, and Sized					
			Plastic Screen		Metal Screen		30- to 60-Micron With a 7.6-Micron Tungsten Coating, WF-270
		Pellets	30- to 60-Micron	< 30-Micron	30- to 60-Micron	< 30-Micron	
Spectrochemical, ppm.*							
Aluminum	10	10	5	10	5	5	-
Boron	-	-	-	-	1	1	-
Chromium	25	25	25	25	25	35	10
Cobalt	1	-	-	-	-	-	
Copper	2	1	1	1	1	5	1
Iron	150	5	10	25	5	10	10
Lead	-	1	5	-	-	-	-
Magnesium	1	120	60	150	10	120	-
Manganese	1	-	-	1	-	1	-
Nickel	5	2	5	5	2	2	10
Silicon	10	1	2	2	1	2	-
Silver	-	-	-	-	-	-	1
Sodium	-	-	1	-	-	-	-
Total	205	165	114	219	50	181	32
Carbon, ppm.			< 4	11			22
Calcium, %			0.70	0.72	0.65	0.69	0.16
Fluoride, ppm.							1,100
Tungsten, %					0.27	0.20	76.3
Uranium, %	86.53		87.44	87.34	87.1	87.1	19.1
O/U Ratio	2.32				2.00	1.99	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in tables II and XVII.

TABLE XI

ANALYTICAL RESULTS FOR URANIUM DIOXIDE CONTAINING 5 MOLE PERCENT CALCIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased from Y-12	UO_2 Containing 5 m/o CaO Sintered at NASA, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	30- to 60-Micron With a 10.3-Micron Tungsten Coating, WF-255
Spectrochemical, ppm.*				
Aluminum	10	25	25	-
Chromium	25	120	120	10
Cobalt	1	2	1	-
Copper	2	60	1	-
Iron	150	200	150	10
Lead	-	10	-	-
Magnesium	1	300	200	1
Manganese	1	5	2	-
Nickel	5	10	5	10
Silicon	10	10	4	1
Tin	-	5	2	-
Zinc	-	60	-	-
Total	205	807	510	32
Tungsten, %				76.7
Uranium, %	86.53	86.98		19.0
O/U Ratio	2.32	2.03		
Fluoride, ppm.				1,900
Carbon, ppm.		76		16
Calcium, %		0.82		

* Listings of elements sought by spectrochemical analysis, together with the limit of detection, are presented in tables II and XVII.

TABLE XII

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 10 MOLE PERCENT CALCIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 10 m/o CaO Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	30- to 60-Micron With an 8.1-Micron Tungsten Coating, WF-262
Spectrochemical, ppm.*				
Aluminum	10	5	5	-
Beryllium	-	-	-	-
Boron	-	-	-	-
Calcium	-	-	-	-
Chromium	25	10	10	-
Cobalt	1	-	-	-
Copper	2	2	1	-
Iron	150	10	25	30
Magnesium	1	150	150	-
Manganese	1	1	2	-
Molybdenum	-	-	-	2
Nickel	5	5	5	-
Silicon	10	3	2	-
Sodium	-	1	-	-
Tantalum	-	-	-	1
Titanium	-	-	-	1
Total	205	187	200	34
Carbon, ppm.		34	8	< 4
Calcium, %		1.48	1.47	0.28
Fluoride, ppm.		-	-	3,900
Tungsten, %		-	-	77.5
Uranium, %	86.53	86.52	86.56	18.2
O/U Ratio	2.32	-	-	-

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in tables II and XVII.

TABLE XIII

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 10 MOLE PERCENT CALCIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 10 m/o CaO Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	30- to 60-Micron With a 9.4-Micron Tungsten Coating, WF-274
Spectrochemical, ppm.*				
Aluminum	10	10	5	-
Boron	-	1	1	-
Cadmium	-	1	1	-
Chromium	25	10	10	-
Cobalt	1	-	-	-
Copper	2	10	1	2
Iron	150	10	5	5
Magnesium	1	150	150	1
Manganese	1	1	-	-
Nickel	5	5	-	-
Silicon	10	-	-	-
Sodium	-	3	-	-
Tin	-	1	-	-
Zirconium	-	-	-	3
Total	205	202	173	11
Carbon, ppm.				6
Calcium, %		1.38	1.33	0.37
Fluoride, ppm.				5,900
Tungsten, %		0.65	0.50	79.3
Uranium, %	86.53	86.0	86.3	16.1
O/U Ratio	2.32	1.97	1.99	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in tables II and XVII.

TABLE XIV

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 5 MOLE PERCENT THORIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 5 m/o ThO_2 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	30- to 60-Micron With a 7.7-Micron Tungsten Coating, WF-278
Spectrochemical, ppm.*				
Aluminum	10	10	10	-
Beryllium	-	3	3	-
Calcium	-	10	10	-
Chromium	25	60	35	-
Cobalt	1	1	-	
Copper	2	5	1	-
Iron	150	150	120	3
Lead	-	5	3	-
Magnesium	1	150	120	-
Manganese	1	1	1	-
Nickel	5	2	2	4
Silicon	10	10	5	-
Sodium	-	10	5	-
Tin	-	1	-	-
Zirconium				5
Total	205	418	315	12
Carbon, ppm.		29	20	9
Fluoride, ppm.				1,320
Tungsten, %		0.87	1.07	75.8
Uranium, %		82.7	82.82	19.7
Thorium, %		4.70	4.39	0.76
O/U Ratio		1.99 ± 0.02	2.00 ± 0.02	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in tables II and XVII.

TABLE XV

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 5 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 5 m/o Y_2O_3 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	30- to 60-Micron With an 8.8-Micron Tungsten Coating, WF-276
Spectrochemical, ppm.*				
Aluminum	10	35	25	-
Calcium	-	50	100	-
Chromium	25	60	35	-
Cobalt	1	-	-	
Copper	2	5	1	1
Iron	150	60	25	15
Magnesium	1	150	120	-
Manganese	1	2	2	-
Nickel	5	2	2	-
Silicon	10	5	2	-
Sodium	-	5	3	-
Titanium				2
Tin	-	1	1	-
Zirconium				5
Total	205	375	316	23
Carbon, ppm.		21	29	4
Fluoride, ppm.				1,300
Tungsten, %		0.56	0.16	79.0
Uranium, %	86.53	83.9	84.3	18.2
Yttrium, %		3.24	3.31	0.91
O/U Ratio	2.32	2.02 ± 0.02	2.00 ± 0.02	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in tables II and XVII.

TABLE XVI

ANALYTICAL RESULTS FOR URANIUM DIOXIDE CONTAINING 5 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased from Y-12	UO_2 Containing 5 m/o Y_2O_3 Sintered at NASA, Ground, and Sized		
		60- to 500-Micron	< 30-Micron	30- to 60-Micron With an 8.5-Micron Tungsten Coating, WF-251
Spectrochemical, ppm.*				
Aluminum	10	30	25	-
Calcium	-	-	200	5
Chromium	25	50	120	10
Cobalt	1	1	-	-
Copper	2	-	35	1
Iron	150	90	200	10
Lead	-	-	10	-
Magnesium	1	50	120	1
Manganese	1	2	5	-
Nickel	5	2	25	5
Silicon	10	2	4	1
Sodium	-	-	5	-
Tin	-	-	5	-
Zinc	-	-	35	-
Total	205	227	789	33
Tungsten, %				75.8
Uranium, %	86.53		80.1	20.7
O/U Ratio	2.32			
Fluoride, ppm.				980
Carbon, ppm.			152	11
Yttrium, %			3.32	

* Listings of elements sought by spectrochemical analysis, together with the limit of detection, are presented in tables II and XVII.

TABLE XVII

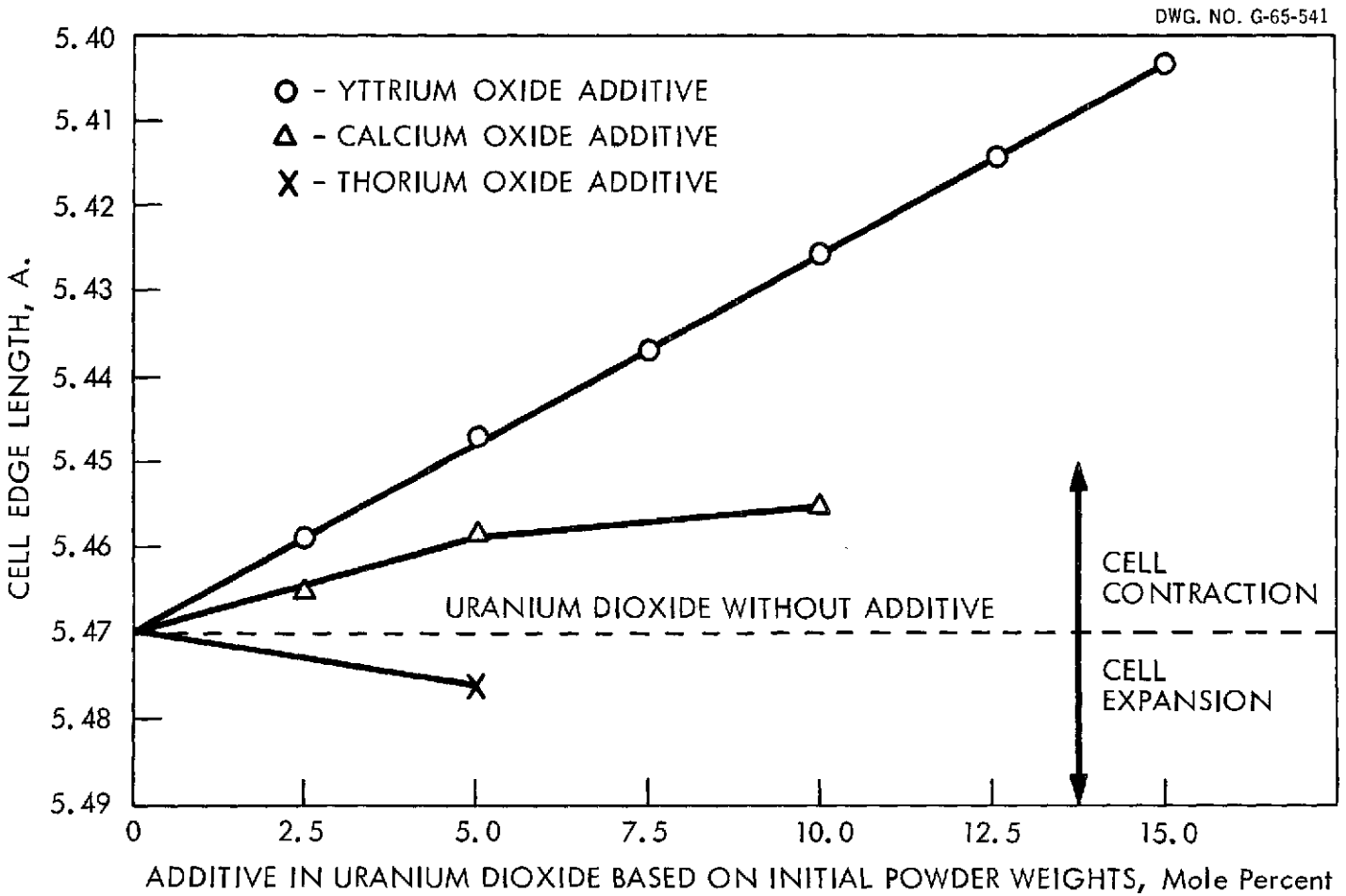
LIMIT OF DETECTION FOR
SPECTROCHEMICAL ANALYSIS OF
TUNGSTEN-COATED URANIUM DIOXIDE

Impurity	Limit of Detection, ppm.
Aluminum	< 1
Beryllium	< 0.1
Bismuth	< 0.5
Calcium	< 1
Chromium	< 1
Copper	< 1
Gallium	< 5
Germanium	< 1
Hafnium	< 2
Iron	< 1
Lead	< 1
Magnesium	< 1
Manganese	< 1
Molybdenum	< 2
Nickel	< 1
Niobium	< 2
Silicon	< 1
Silver	< 1
Sodium	< 1
Tantalum	< 4
Thallium	< 1
Tin	< 1
Titanium	< 2
Vanadium	< 2
Zinc	< 10
Zirconium	< 2

TABLE XVIII

COMPARISON OF ADDITIVE CONCENTRATION DATA

Additive	Sample Number	Additive in UO_2, mole percent: Based on Initial Powder Weights	Additive in UO_2, mole percent: Determined by Chemical Analysis
CaO	WF-271	2.5	2.45
CaO	WF-255	5.0	5.31
CaO	WF-274	10.0	8.41
Y_2O_3	WF-251	5.0	5.56
Y_2O_3	WF-276	5.0	4.91
ThO_2	WF-278	5.0	5.50
Y_2O_3	K-256	2.5	2.54
Y_2O_3	K-245	5.0	5.28
Y_2O_3	K-250	7.5	7.86
Y_2O_3	K-243	10.0	10.30
Y_2O_3	K-252	12.5	12.40
Y_2O_3	K-254	15.0	14.70



DEPENDENCE OF CELL EDGE LENGTH DETERMINED BY X-RAY DIFFRACTION ON COMPOSITION OF URANIUM DIOXIDE-ADDITIVE SOLID SOLUTIONS

Figure 18

Preparation of the Second Series of NASA Samples

The objective of the second phase of task 6 was the preparation of 1-pound samples of 30- to 60-micron uranium dioxide containing 2-1/2, 5, 7-1/2, 10, 12-1/2, and 15% yttrium oxide in solid solution. A control sample which contained no yttrium oxide was to be prepared by the same method. These powders were produced in the amounts shown in table XIX by the techniques used for the first set of NASA samples. As the final step, the powder was placed in the vapor plating reactor and was fluidized with helium at room temperature. The fluidization operation was successful in removing fine particulate contaminants, such as magnesium, iron, etc., which had been picked up in the grinding and sizing operations. In most cases, this elutriation resulted in a sizable improvement in product purity.

Analytical results on the yttrium oxide used in these preparations appear in table XX. The results of analyses on the samples prepared for NASA are presented in tables XXI through XXVII. For the 30- to 60-micron powder, the total detectable metallic impurities vary between 19 and 143 ppm., and the carbon contents range from 6 to 21 ppm. All samples meet the specifications; i.e., they contain less than 300 ppm. total detectable impurities other than tungsten. The oxygen-to-uranium ratios for the fines ranged from 1.97 to 2.07. Again, it must be emphasized that these calculated oxygen-to-uranium ratios are open to question because of the undetermined effects of the tungsten contaminants and the stoichiometry of the yttria additives. Moreover, the results are not very precise since the oxygen is obtained by difference and could be influenced by the errors in the three independent analyses for uranium, tungsten, and yttrium. In fact, an error of 0.1% in any one of these analyses would cause an error of 1% in the oxygen-to-uranium ratio.

Preparation of Fine By-Product

The preparation of 30- to 60-micron powders for the first and second series resulted in the product of less than 30-micron by-product powder in the amounts shown in table XXVIII. Analytical results for this fine by-product from the first series were presented in tables VII through XVI. The metallic impurities in these powders were often much higher than for the in-size powders, ranging from 310 to 890 ppm. The magnesium content of these samples was particularly high. It is suspected that the source of this contaminant was airborne magnesia particles present in the laboratory atmosphere. With one exception, the carbon content was only slightly higher than that of the 30- to 60-micron product, ranging from 11 to 34 ppm. There was also good agreement between the in-range and by-product powders on stoichiometry and additive concentration.

Improvements in powder handling techniques lower the detectable metallic impurity contents in the fine by-products from the second series to the 181 to 287 ppm. range. The carbon contents of these powders varied from 9 to 25 ppm. Excluding tungsten, which is acceptable at high levels, these fine by-products would meet a specification of 300 ppm. total detectable metallics.

TABLE XIX

PREPARATION OF 30- TO 60-MICRON URANIUM DIOXIDE CONTAINING YTTRIUM OXIDE IN SOLID SOLUTION

Y_2O_3 Concentration, mole percent	Sample Number	Amount Prepared, grams
0 (Control)	K-246	553
2-1/2	K-256	408
5	K-244	649
7-1/2	K-250	495
10	K-242	530
12-1/2	K-252	429
15	K-254	267

TABLE XX

SPECTROCHEMICAL ANALYSIS OF YTTRIUM OXIDE

Element	Vendor Analysis, ppm.	ORGDP Analysis, ppm.
Aluminum	< 6	< 5
Calcium	< 10	20
Iron	< 12	< 5
Magnesium	< 4	< 5
Rare Earths	< 10	ND
Silicon	< 36	< 5

TABLE XXI

ANALYTICAL RESULTS FOR URANIUM DIOXIDE CONTAINING NO ADDITIVE (CONTROL)

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing No Additive Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	
			As-Screened	After Elutriation
Spectrochemical, ppm.*				
Aluminum	2	25	25	10
Beryllium	-	5	5	5
Boron	-	-	-	-
Calcium	5	5	5	-
Chromium	5	5	5	5
Cobalt	-	-	-	-
Copper	10	10	1	1
Iron	20	5	5	10
Magnesium	-	120	120	100
Manganese	-	-	-	-
Nickel	10	-	-	5
Silicon	5	3	2	4
Sodium	1	3	1	-
Tin	1	-	-	-
Zinc	60	-	-	-
Total	119	181	169	140
Carbon, ppm.		18	8	
Fluoride, ppm.	80	-	-	
Tungsten, %		1.45	0.75	
Uranium, %	87.56	86.7	86.6	
O/U Ratio	2.14	2.03 ± 0.05	2.05 ± 0.02	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in table II.

TABLE XXII

ANALYTICAL RESULTS FOR URANIUM DIOXIDE CONTAINING 2.5 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 2.5 m/o Y_2O_3 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	
			As-Screened	After Elutriation
Spectrochemical, ppm.*				
Aluminum	2	25	60	10
Beryllium	-	3	3	2
Boron	-	-	-	-
Calcium	2	5	5	-
Chromium	25	25	25	10
Cobalt	-	1	1	-
Copper	10	1	1	2
Iron	35	20	20	10
Magnesium	1	150	150	100
Manganese	1	2	2	-
Nickel	10	2	2	5
Silicon	5	1	1	4
Sodium	-	-	5	-
Tin	-	2	-	-
Zinc	35	35	-	-
Total	126	272	275	143
Carbon, ppm.	14	26	21	
Yttrium, %	-	1.70	1.76	
Fluoride, ppm.	-	-	-	
Tungsten, %	-	0.97	0.80	
Uranium, %	87.35	85.4	85.5	
O/U Ratio	2.14	2.00 ± 0.05	2.01 ± 0.05	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in table II.

TABLE XXIII

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 5 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 5 m/o Y_2O_3 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	
			As-Screened	After Elutriation
Spectrochemical, ppm.*				
Aluminum	2	5	2	5
Beryllium	-	5	5	5
Boron	-	-	-	-
Calcium	5	2	2	-
Chromium	5	10	10	10
Cobalt	-	-	2	-
Copper	10	25	1	2
Iron	20	10	10	5
Magnesium	-	150	150	20
Manganese	-	2	1	-
Nickel	10	2	2	5
Silicon	5	1	1	2
Sodium	1	3	3	1
Tin	1	-	-	-
Zinc	60	-	-	-
Total	119	215	189	55
Carbon, ppm.		9	7	
Yttrium, %		3.16	3.44	
Fluoride, ppm.	80	-	-	
Tungsten, %		1.99	1.74	
Uranium, %	87.56	82.6	82.4	
O/U Ratio	2.14	2.06 ± 0.05	1.95 ± 0.05	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in table II.

TABLE XXIV

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 7.5 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 7.5 m/o Y_2O_3 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	
			As-Screened	After Elutriation
Spectrochemical, ppm.*				
Aluminum	2	10	5	5
Beryllium	-	5	5	3
Boron	-	-	-	-
Calcium	2	10	10	-
Chromium	25	25	10	5
Cobalt	-	1	2	-
Copper	10	35	1	1
Iron	35	10	5	-
Magnesium	1	150	35	20
Manganese	1	2	-	-
Nickel	10	2	2	5
Silicon	5	1	1	1
Sodium	-	1	-	-
Tin	-	-	-	-
Zinc	35	35	35	-
Total	126	287	111	40
Carbon, ppm.	14	14	6	
Yttrium, %	-	5.05	5.16	
Fluoride, ppm.	-	-	-	
Tungsten, %	-	1.60	0.075	
Uranium, %	87.35	81.2	80.9	
O/U Ratio	2.14	1.97 ± 0.05	2.04 ± 0.05	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in table II.

TABLE XXV

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 10 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 10 m/o Y_2O_3 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	
			As-Screened	After Elutriation
Spectrochemical, ppm.*				
Aluminum	2	5	-	2
Beryllium	-	5	5	3
Boron	-	1	1	-
Calcium	5	1	1	
Chromium	5	10	5	2
Cobalt	-	1	2	2
Copper	10	25	1	-
Iron	20	35	10	5
Magnesium	-	150	25	5
Manganese	-	2	1	-
Nickel	10	5	5	5
Silicon	5	2	2	2
Sodium	1	3	3	1
Tin	1	-	-	-
Zinc	60	-	-	-
Total	119	245	61	27
Carbon, ppm.		15	16	
Yttrium, %		6.59	6.69	
Fluoride, ppm.	80	-	-	
Tungsten, %		1.73	1.54	
Uranium, %	87.56	79.1	77.8	
O/U Ratio	2.14	2.04 ± 0.05	1.94 ± 0.05	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in table II.

TABLE XXVI

ANALYTICAL RESULTS FOR URANIUM DIOXIDE
CONTAINING 12.5 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 12.5 m/o Y_2O_3 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	
			As-Screened	After Elutriation
Spectrochemical, ppm.*				
Aluminum	2	5	2	-
Beryllium	-	5	5	3
Boron	-	-	-	-
Calcium	2	2	2	-
Chromium	25	10	5	5
Cobalt	-	1	2	-
Copper	10	35	1	-
Iron	35	20	-	-
Magnesium	1	120	25	5
Manganese	1	2	1	-
Nickel	10	5	2	5
Silicon	5	2	1	1
Sodium	-	1	1	-
Tin	-	1	-	-
Zinc	35	35	-	-
Total	126	244	47	19
Carbon, ppm.	14	10	20	
Yttrium, %	-	8.20	8.52	
Fluoride, ppm.	-	-	-	
Tungsten, %	-	1.64	0.90	
Uranium, %	87.35	77.2	76.4	
O/U Ratio	2.14	2.07 ± 0.05	2.04 ± 0.05	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in table II.

TABLE XXVII

ANALYTICAL RESULTS FOR URANIUM DIOXIDE CONTAINING 15 MOLE PERCENT YTTRIUM OXIDE

Element	Ceramic-Grade UO_2 Purchased From Y-12	UO_2 Containing 15 m/o Y_2O_3 Sintered at Y-12, Ground, and Sized		
		< 30-Micron	30- to 60-Micron	
			As-Screened	After Elutriation
Spectrochemical, ppm.*				
Aluminum	2	5	2	2
Beryllium	-	10	10	5
Boron	-	1	1	-
Calcium	2	2	1	-
Chromium	25	10	5	1
Cobalt	-	1	2	-
Copper	10	35	1	1
Iron	35	10	5	-
Magnesium	1	120	25	5
Manganese	1	2	-	-
Nickel	10	5	2	3
Silicon	5	2	1	2
Sodium	-	1	-	1
Tin	-	1	-	-
Zinc	35	35	-	-
Total	126	240	55	20
Carbon, ppm.	14	25	< 10	
Yttrium, %	-	9.88	10.16	
Fluoride, ppm.	-	-	-	
Tungsten, %	-	2.13	1.08	
Uranium, %	87.35	74.9	74.3	
O/U Ratio	2.14	2.07 ± 0.05	2.02 ± 0.05	

* Listings of elements sought by spectrochemical analysis, together with the limits of detection, are presented in table II.

TABLE XXVIII

FINE BY-PRODUCT POWDER

Additive	Additive Concentration, mole percent	Sample Number	Amount Prepared, grams
		First Series	
Control	0	K-151, K-172	581
Calcium Oxide	2-1/2	K-145, K-174	907
Calcium Oxide	5	K-150, K-168, K-170, K-184	755
Calcium Oxide	10	K-157, K-161, K-193	1,073
Thorium Oxide	5	K-180, K-203	1,400
Yttrium Oxide	5	K-144, K-195	706
		Second Series	
Control	0	K-247	866
Yttrium Oxide	2-1/2	K-257	709
Yttrium Oxide	5	K-245	831
Yttrium Oxide	7-1/2	K-251	923
Yttrium Oxide	10	K-243	827
Yttrium Oxide	12-1/2	K-253	865
Yttrium Oxide	15	K-255	714

CONCLUSIONS

In summary, a 2-pound sample of spheroidized 30- to 60-micron uranium dioxide has been prepared by a plasma jet technique for the NASA Lewis Research Center. The product, which had an oxygen-to-uranium ratio of 2.000 to 1, contained less than 50 ppm. detectable metallics. Scale-up of the spheroidization process has increased throughput rates by a factor of 6 and has decreased product cost by an order of magnitude.

Pound lots of tungsten-coated, 30- to 60-micron uranium dioxide with calcium oxide, thorium oxide, and yttrium oxide in solid solutions have been produced for NASA. Total detectable metallics in the coated product were in the 20- to 40-ppm. range; however, some fluoride contamination occurred during vapor plating.

Pound lots of 30- to 60-micron uranium dioxide containing various concentrations of yttrium oxide in solid solution were also prepared. Total impurity content was within the 300 ppm. specification.

Finally, exploratory studies were performed on methods for preparing ultrafine uranium dioxide powders, and a 1-pound sample of uranium dioxide containing 10% yttrium oxide was ground to an average size of 2.4 microns.

ACKNOWLEDGEMENTS

The authors are indebted to S. H. Smiley and W. E. Tewes for suggestions and advice and for guidance in the management of the technical programs. Acknowledgement is made to the Works Laboratory for performance of the various analyses used in this report.

BIBLIOGRAPHY

(1) Gedwill, M. A., Sikora, P. R., and Caves, R. M., Fuel Retention Properties of Tungsten-Uranium Dioxide Composites, NASA Lewis Research Center, February, 1965 (NASA TM X-1059).

NOTEBOOK REFERENCES

1. Knight, R. G., ORGDP Research Notebook Number 4895.

2. Stanley, F. S., ORGDP Research Notebook Number 4696.

3. Stanley, F. S., ORGDP Research Notebook Number 4804.

PART II

CLADDING AND JOINING OF TUNGSTEN CERMETS BY PLASMA SPRAYING (U)

By

W. L. Cochran
R. G. Knight
F. S. Stanley

Engineering Development Department
Technical Division

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

(Identification C-25101A)

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Materials and Structures Division
Robert M. Caves

Part II: CLADDING AND JOINING OF TUNGSTEN CERMETS BY PLASMA SPRAYING

SUMMARY

A series of nine test specimens of tungsten-uranium dioxide cermet fuel elements was edge-coated with a layer of tungsten by spraying with the SG-3 plasma torch at a power level of 24 kw. with a nitrogen-hydrogen plasma. A torch-to-work distance of 1-1/4 inches and a traverse speed of 76 inches per minute produced a very high density coating which was metallurgically bonded to the substrate; however, this cladding failed to retain all the uranium dioxide when the test specimens were evaluated at elevated temperatures at NASA. Microscopic examination of the samples after testing indicated that the uranium dioxide loss may have been associated with uranium dioxide which melted during plasma spraying and which was deposited at the interface or along tungsten grain boundaries in the cladding, thus providing a diffusion path to the surface where evaporation could occur. Coating reproducibility may also have been a problem.

Additional development studies were conducted in an effort to improve the plasma spray edge coating technique. Emphasis was placed on establishment of reproducible spray conditions which would not melt the uranium dioxide but which would produce a dense, metallurgically bonded coating. A number of changes were made to equipment and operating conditions in an effort to improve the reliability and reproducibility of the plasma spraying process. Because of the difficulty with electrode wear experienced previously when operating the SG-3 torch at its rated capacity with a nitrogen-hydrogen plasma, emphasis was placed on the use of the SG-1 helium plasma system for the tungsten edge coating work. To minimize electrode wear, the larger SG-1 plasma torch was operated well below its rated capacity.

Based on generally encouraging results, five sets of samples were prepared for high temperature tests at the NASA Lewis Research Center. For these tests, 3 to 4 mils of tungsten was plasma-sprayed on each edge of tungsten-uranium dioxide fuel elements. Torch-to-work distances of 1-3/4, 1-7/8, and 2 inches and a traverse speed of 30 inches per minute were used with the SG-1 plasma torch operating at a power level of 24 kw. Helium was used both as the arc gas and as the powder feed gas, while hydrogen was introduced into the plasma through the powder port of the front electrode. Hydrogen was also added to the cover gas in the spray chamber to provide a reducing atmosphere. Tungsten-uranium dioxide test coupons prepared as controls with the test samples showed good coverage and good bonding when examined metallographically. The test samples were shipped to NASA for evaluation in high temperature, fuel retention tests. The results indicated that the edge coatings on all samples were effective in preventing fuel loss at elevated temperatures.

While the main effort was spent on edge coating, scoping studies were run on (a) coating the entire surface of flat fuel elements, (b) the formation of T-joints by plasma spraying, and (c) the formation of fuel joints

by codeposition of tungsten and uranium dioxide. Some encouragement was obtained from the latter series of tests, since a fully dense deposit was achieved; however, further development is needed to prevent melting of uranium dioxide during spraying, since the molten uranium dioxide was deposited along the tungsten grain boundaries.

INTRODUCTION

This project, which was a continuation and an extension of work conducted during fiscal year 1964, had two broad objectives: (a) the development of methods for tungsten coating tungsten-uranium dioxide cermet fuel elements by plasma spraying, and (b) the development of methods for joining tungsten-uranium dioxide cermets by plasma spraying. The goal of the cladding studies was to develop a fully dense, impervious, metallurgically bonded tungsten coating which would prevent evaporative loss of the uranium dioxide fuel from the cermet at the proposed operating temperature of a nuclear powered rocket[1,2]. The second phase of the work was aimed at the development of a pore-free, metallurgically bonded, plasma-sprayed tungsten joint at least as strong as the tungsten-uranium dioxide cermet at reactor operating temperatures. Representative samples from each study were to be submitted to NASA for testing and evaluation in connection with materials research for the tungsten water-moderated nuclear rocket concept under study at the NASA Lewis Research Center.

Several specific investigations were scheduled in each area. The cladding work included (a) the preparation, by techniques developed last fiscal year, of edge-coated cermets for environmental testing at NASA; (b) perfection of the edge coating process to obtain improved retention of the uranium dioxide at high temperatures; and (c) scoping studies on plasma coating the entire surface of flat cermet fuel elements. The joining effort included (a) scoping work on the preparation of T-joints, and (b) exploratory studies on the preparation of fueled joints by the codeposition of tungsten and uranium dioxide.

CLADDING STUDIES

Early in the current fiscal year, a group of nine tungsten-uranium dioxide cermet samples was edge-coated and was shipped to NASA for high temperature testing. While these tests were in progress, a few scoping studies were performed to determine the problems involved with plasma coating the flat surface of a fuel element. When excessive fuel loss was encountered with the edge-coated samples in the environmental tests at NASA, the work was redirected toward improvement of the edge coating process. At the request of NASA, the entire effort on this project was concentrated on edge coating for the rest of the fiscal year.

Preparation of Initial Edge-Coated Test Specimens

The objective of the edge coating studies was to establish plasma spray conditions which could be used to apply pore-free, metallurgically bonded

tungsten onto tungsten-uranium dioxide fuel elements to encapsulate completely and to contain the uranium dioxide when the fuel element is operated at nuclear reactor temperatures. Metallurgical examination of samples prepared during fiscal year 1964 indicated that a very high density coating with excellent bonding had been achieved. The conditions established during these tests were then used to coat the edges of nine 3/4-inch by 3-inch samples which were used for thermal cycling tests at NASA. The following coating procedures were employed:

1. Each sample was polished with 400-grit silicon carbide abrasive cloth, followed by an acetone rinse.

2. Each sample was positioned in the controlled atmosphere chamber where the atmosphere was changed by pumping out the air and backfilling with argon.

3. At a torch-to-work distance of 1-1/4 inches, the sample was traversed for two passes at 76 inches per minute in front of the SG-3 plasma torch which was operated at 24 kw. with a nitrogen-hydrogen arc gas mixture. Minus 270 plus 325-mesh tungsten powder was conveyed to the torch with argon as the carrier gas. After cooling, the sample was repositioned, and the other edges were coated in the same way. The test specimen was then removed from the chamber.

The flat faces of the samples had a dull appearance as if surface oxidation had occurred after shutdown of the plasma torch; however, neither reduction in hydrogen at 1600°C. nor vacuum treatment at 1700°C. improved the appearance of the samples. X-ray diffraction analyses indicated that the dull appearance was due to a thin layer of tungsten which condensed on the samples during plasma coating. This layer, which was only loosely adherent, could be removed by vigorous rubbing or by an additional pass through the torch; however, it should not affect the characteristics of the coating.

The samples prepared using the above techniques failed to retain the uranium dioxide when tested at elevated temperatures at NASA. Microscopic examination of the samples after thermal cycling indicated that the fuel loss may have been caused by uranium dioxide which melted during spraying and redeposited along the interface between the cladding and the substrate or in the grain boundaries of the cladding, thus providing a diffusion path to the surface where evaporation could occur. Even though previous inspection of sectioned samples prepared at the same conditions as the test samples had shown consistently good metallurgical bonding of the applied coating to the substrate, most sections of the nine samples showed generally poor bonding after testing at elevated temperatures. The loss of uranium dioxide from the interface could give the appearance of poor bonding.

These data indicate that metallurgical inspection of the coated and sectioned samples cannot always be relied upon to predict uranium losses at elevated temperatures. It should be pointed out, however, that it was not possible to inspect metallographically the same samples before

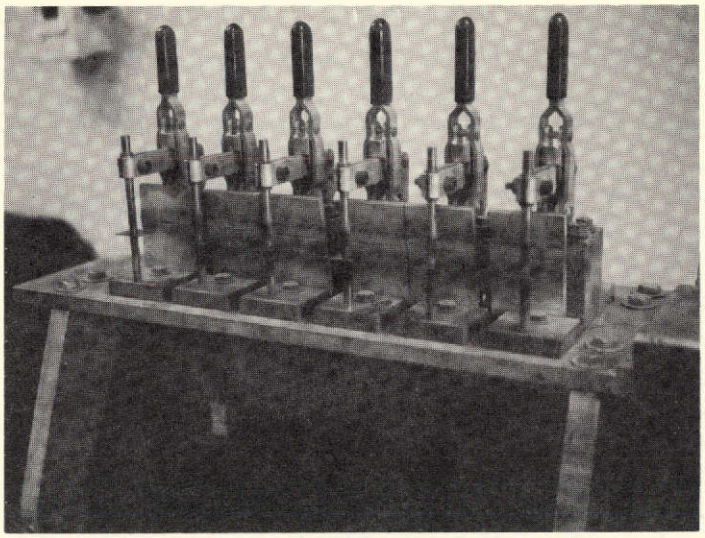
and after heat treatment; and due to the scarcity of material, control samples were not prepared along with the nine test samples. Thus, although coating conditions were maintained as consistently as possible, some variation from established procedures could have been a factor which contributed to the coating failure during testing at NASA. In any case, it was apparent from the results of environmental testing that additional development was needed on the edge coating process.

Edge Coating with the SG-3 Nitrogen-Hydrogen Plasma System

The first phase of the development program was initiated using the same plasma spray system employed for the preparation of the NASA test samples. Based on Grisaffe's observations[1], a series of tests designed to produce a wide range of substrates and particle temperatures was started, although neither of these temperatures was amenable to direct measurement. This was accomplished by varying the torch-to-work distance and the traverse speed, both of which control the substrate temperature and the coating powder feed rate which, along with the torch-to-work distance, would affect the particle temperature. Although several conditions were found at which metallurgical bonding was achieved with essentially no uranium dioxide melting, subsequent samples prepared at the same conditions did not show consistently comparable results. One evident reason for this was the changing power level caused by short electrode life of the SG-3 90% nitrogen-10% hydrogen plasma system. At 24 kw., this system was operating at its maximum capacity, and with the erosive nitrogen-hydrogen plasma, severe electrode wear occurred, particularly in the region near the foot point of the arc. As the electrodes wore, the power level would drop rapidly, sometimes falling as much as 10% while two samples were being coated. In view of this excessive electrode wear, the SG-3 nitrogen-hydrogen system did not appear suitable for a practical edge coating operation.

Edge Coating with the SG-1 Helium Plasma System

The SG-1 helium plasma system had been used successfully in spraying tungsten powder and had operated for extended periods without serious electrode erosion. Since uniform operation from day to day was a prime goal, this system was selected for the edge coating development equipment. Coincident with the selection of the SG-1 helium plasma system, the edge coating operation was moved into a new, water-cooled, 2-foot diameter by 4-foot long controlled atmosphere spray chamber. The chamber has remote facilities for moving the torch inside the chamber, and the atmosphere is filtered continuously and is cooled by recirculation. To facilitate the preparation of a larger number of samples, the six-position sample holder, shown in figure 1, was fabricated and used. Tungsten rods hold the pieces being edge coated, and each of the six holders is independently adjustable. This feature permitted up to six different torch-to-work distances to be tested in a single plasma spray pass.



SIX-POSITION SAMPLE HOLDER
(20 inches x 16 inches x 6 inches)

Figure 1

Plasma Operating Conditions

Since it was concluded that the bonding might be affected by any number of combinations of power settings, gas compositions, torch-to-work distances, or traverse speeds, the first efforts were directed toward elimination of as many variables as possible by stabilizing the plasma arc operating conditions. The SG-1 torch, which has a rated capacity of 40 kw., was operated at a power level of 24 kw. With helium as the arc gas, this power level was obtained using operating voltages of 50 and a current of 480 amperes. The flow of the helium arc gas was fixed at 70 liters per minute, while the helium powder gas flow was regulated at 2 liters per minute. Hydrogen was introduced through the powder port at a rate of 7 liters per minute to provide a reducing atmosphere.

Using the specified parameters and the equipment described previously, an experimental program was started to determine the range of other process variables which would produce the most effective conditions for accomplishing the edge coating. Since none of the variables acted independently of the others, most phases of the program were conducted simultaneously.

Chamber Atmosphere. In the initial tests within the new controlled atmosphere chamber, it was found that chamber gas composition had an effect on the torch-to-work distance required to achieve acceptable bonding. Premixed 90% argon-10% hydrogen was used as the chamber gas, and the helium plasma generated under these conditions had a relatively long and bushy appearance. It was observed, however, that the appearance of the plasma would change gradually as the torch continued to run due to dilution of the argon atmosphere with helium. Apparently some of the argon was being ionized along the edges of the helium plasma, and this ionized sheath tended to extend the plasma zone. To ensure a constant plasma over an extended period, all subsequent tests were made with a chamber atmosphere of the same composition as the gases fed to the plasma gun; i.e., about 9% hydrogen in helium. It was found that, where a 2-1/2-inch torch-to-work distance produced an acceptable bond using argon-hydrogen in the chamber, a torch-to-work distance of about 2 inches was required when helium and hydrogen were used.

Torch-to-Work Distance and Traverse Speed. Traverse speeds of 10, 20, 40, and 80 inches per minute were used to prepare samples in triplicate at torch-to-work distances ranging from 1-1/2 to 2-3/4 inches for metallurgical examination. The sectioned samples were examined for bonding, thermal history, effectiveness of precoating clean-up, and general appearance of the coating.

It was anticipated in the design of this experiment that a bonding zone would be established with respect to distance and traverse speed. The results indicated that, at both 20 and 40 inches per minute, good bonding could be achieved with about 1/4-inch variation in the torch-to-work distance. Uranium dioxide melting occurred on most of the samples produced at 10 inches per minute, and no bonding took place on the samples prepared at 80 inches per minute. The best bonds were obtained at the

extreme distance tested at the 20-inch per minute traverse speed and at the closest distance tested at 40 inches per minute.

The traverse speed was then stabilized at 30 inches per minute, and using the plasma operating conditions described previously, additional samples were prepared. These tests established that good bonding occurred at a torch-to-work distance between 1-3/4 and 2 inches. Some very slight uranium dioxide melting was observed at 1-3/4 inches, and bonding was less than 100% at 2-1/8 inches.

Sample Clean-Up Conditions. Prior to the actual coating operation, the plasma torch was traversed across the edge which was to be coated to remove surface impurities. For this clean-up operation, the power level and all gas flows were maintained at the same level as for coating.

Metallographic examination of a large number of samples revealed that conditions of good bonding were frequent, but in almost every set of samples, poorly bonded zones occurred adjacent to zones of good bonding without any apparent or easily recognized reason. The general appearance of the samples led to the conclusion that surface impurities were probably responsible for the poorly bonded zones. The clean-up procedure was made more rigorous by decreasing the torch traverse speed from 80 inches per minute to 40 inches per minute and by making two clean-up passes instead of one. At these conditions, good bonding occurred most of the time, and a clean-up system to purify the hydrogen being used improved the bonding consistency even more.

Powder Feed Rate. One of the major problem areas was establishing the powder feed rate required to achieve an even coating thickness consistently. Even with constant powder feed rates, very slight variations in flame geometry, torch-to-work distance, or traverse speed would produce measurable differences in the coating thickness. At fixed feed hopper settings and powder gas flows, the feed rate was also observed to fluctuate with slight changes in chamber pressure, variations in powder size, and moisture content of the powder.

To circumvent this problem, procedures were established for drying, screening, and installing a fresh powder charge for each run; the powder gas flow was set at a fixed value; and with the gun operating, the feed rate was observed by two experienced operators. Any adjustments required to obtain consistent, apparent feed rates were made by changing the vibrator setting or by very minor changes in the gas flow. Using this system with minus 230 plus 325-mesh powder, 1-1/2 mils per pass was consistently sprayed at the established operating conditions. Attempts to measure this feed rate indicated a rate of about 8 grams per minute.

Powder Size. Tests were made to determine the effect of powder size on the bonding, grain size, and general appearance of the coating. Of the powders tried, both a minus 230 plus 325-mesh powder and a minus 325 plus 400-mesh powder appeared to yield the best and most consistent results. Either powder had to be dry and well screened to feed properly. There was no apparent difference in the quality of coating between these two

powders, but at the same plasma operating conditions, three coating passes were required with the smaller powder to achieve the same coating as achieved in two passes using the large powder.

Preparation of Edge-Coated Test Coupons for NASA

Samples 1-3/8 inches long by 11/16 inch wide were cut to size from stock furnished by NASA using a 120-grit, rubber bonded, glass cut-off wheel. Attempts to perform the operation with a mechanical feed were unsuccessful, and cutting had to be done with manual feed where the feed pressure could be held fairly constant. The following precedures were used in coating the test coupons.

1. Each sample was cleaned for 10 minutes in an ultrasonic cleaner using methanol as the solvent immediately prior to the coating operation.

2. Each set of samples was then positioned in the controlled atmosphere chamber, along with the control samples. The chamber atmosphere was changed by pumping with an air jet to a vacuum of 27 inches of mercury and backfilling with helium. This operation was performed three times. On the third and final backfill, hydrogen was added with the helium backfilling gas to provide a reducing atmosphere around the samples while they were being coated.

3. At a torch-to-work distance predetermined for the set of samples, the torch was traversed at 40 inches per minute across the samples for two clean-up passes. The SG-1 plasma torch was then operated at 24 kw. with a helium plasma arc gas and a traverse speed of 30 inches per minute.

4. After cooling, the samples were removed from the chamber and were repositioned, and the other edges were coated in the same way.

Table I shows the coating thicknesses which were applied to each of the edges of each sample as determined by micrometer measurements, while table II shows the conditions used during each coating run. Control specimens were prepared for each spray run and were examined metallographically. Photomicrographs of the coated samples representing the various sets are shown as figures 2 through 6. It can be observed that the torch-to-work distance of 1-3/4 inches resulted in some uranium dioxide melting, indicating too high a substrate temperature. The photomicrographs were taken on control specimens which were not necessarily from the same tungsten-uranium dioxide cermet stock as the samples actually tested at NASA.

Results of Tests at NASA

Table III shows the preliminary results of the tests which were conducted at elevated temperatures at NASA. These results indicate that the coating applied by these techniques was very effective in the reduction of uranium loss from the samples at the proposed reactor operating temperatures.

TABLE I

TUNGSTEN COATING APPLIED TO TUNGSTEN-URANIUM DIOXIDE CERMET EDGES BY PLASMA SPRAYING

Set Number	Sample Number	Torch-to-Work Distance, in.	Passes		Coating Thickness, mils*			
			Clean-Up	Work	Side 1	Side 2	Side 3	Side 4
1	C-1†	1-3/4	2	2	4.7 to 6.3	5.5 to 5.9	2.2 to 2.9	4.8 to 4.8
	C-2				2.7 to 3.9	4.9 to 6.2	3.4 to 4.5	4.6 to 4.9
	C-3				3.8 to 4.1	4.6 to 4.9	3.7 to 3.8	4.7 to 4.9
	C-4				2.8 to 3.4	5.7 to 5.8	3.8 to 3.9	5.4 to 6.3
	C-5				3.3 to 3.7	6.1 to 6.2	4.0 to 4.8	5.4 to 6.7
	C-6†				4.2 to 6.5	6.8 to 6.9	3.5 to 3.8	6.8 to 7.7
2	2-C-1†	1-7/8	2	2	3.0 to 3.0	4.0 to 4.2	4.5 to 4.7	3.2 to 4.2
	2-C-3				2.5 to 3.0	4.1 to 4.3	3.5 to 4.0	3.2 to 4.4
	2-C-4				3.5 to 3.7	4.0 to 4.0	4.3 to 4.5	4.0 to 4.1
	2-C-6†				3.1 to 3.1	4.0 to 4.6	4.1 to 4.8	3.8 to 4.2
3	3-C-2	2	2	3	3.1 to 5.3	0.5 to 2.7	2.3 to 2.9	3.3 to 4.0
	3-C-3				2.6 to 3.6	2.0 to 3.0	2.5 to 2.9	4.1 to 4.3
	3-C-4				3.1 to 5.0	1.0 to 1.7	2.0 to 2.5	2.7 to 4.5
	3-C-5†				2.5 to 2.9	1.0 to 2.0	2.5 to 2.7	2.8 to 4.2
4	4-C-2	2	2	3	5.3 to 6.6	3.3 to 4.9	3.9 to 4.0	3.8 to 4.4
	4-C-3				6.0 to 7.0	3.9 to 5.2	3.1 to 3.5	4.8 to 5.2
	4-C-4				5.0 to 5.7	5.5 to 6.3	5.8 yo 6.7	4.9 to 5.1
	4-C-5†				5.8 to 7.0	3.0 to 3.3	4.4 to 4.4	4.4 to 5.0
5	5-C-2	2	2	3	3.7 to 4.0	2.8 to 3.9	3.3 to 4.4	3.0 to 4.4
	5-C-3				4.2 to 4.9	2.7 to 3.0	4.0 to 4.2	4.0 to 5.5
	5-C-4				3.9 to 4.0	2.1 to 3.0	3.7 yo 4.3	4.1 to 4.5
	5-C-5				4.0 to 4.2	3.1 to 3.9	5.5 to 5.6	4.4 to 4.4

* Results of duplicate measurements.

† Samples sectioned at ORGDP. Other samples delivered to NASA.

Note: Sets 1, 2, 4, and 5 were sprayed with minus 230 plus 325-mesh tungsten powder. Set 3 was sprayed with minus 325 plus 400-mesh tungsten powder.

TABLE II

OPERATING CONDITIONS FOR SG-1 PLASMA GENERATOR DURING PREPARATION OF EDGE-COATED SAMPLES TESTED AT NASA

Run Number	Running Time on Front Electrode*, min.	Operating Voltage†, v.	Current, amp.	Power, kw.	Torch-To-Work Distance, in.	Gas Flows, l./min.		
						Helium Arc Gas	Hydrogen Cover Gas	Helium Powder Gas
RC-1	219	50	480	24.0	1-3/4	70	7.10	2.20
C-1	88	49	490	24.0	1-3/4	69	6.90	2.60
C-2	137	52	460	23.9	1-3/4	69	6.90	2.60
C-3	152	51	470	24.0	1-3/4	69	6.90	2.20
C-4	165	51	470	24.0	1-3/4	71	7.10	1.50
2-C-1	233	49	490	24.0	1-7/8	69	7.10	2.20
2-C-2	251	52	470	24.4	1-7/8	69	7.10	1.19
2-C-3	260	51	470	24.0	1-7/8	72	7.10	1.18
2-C-4	273	50	480	24.0	1-7/8	71	7.10	1.50
3-C-1‡	96	50	480	24.0	2	69	7.15	0.95
3-C-2‡	111	50	480	24.0	2	69	7.15	0.68
3-C-3‡	127	50	480	24.0	2	69	6.90	0.51
3-C-4‡	138	49	490	24.0	2	69	7.15	0.68
4-C-1	183	52	460	23.9	2	71	7.15	1.44
4-C-2	206	51	450	23.0	2	71	7.20	1.44
4-C-3	217	50	480	24.0	2	71	6.90	1.44
4-C-4	231	46	520	23.9	2	70	7.15	1.03

TABLE II (Contd.)

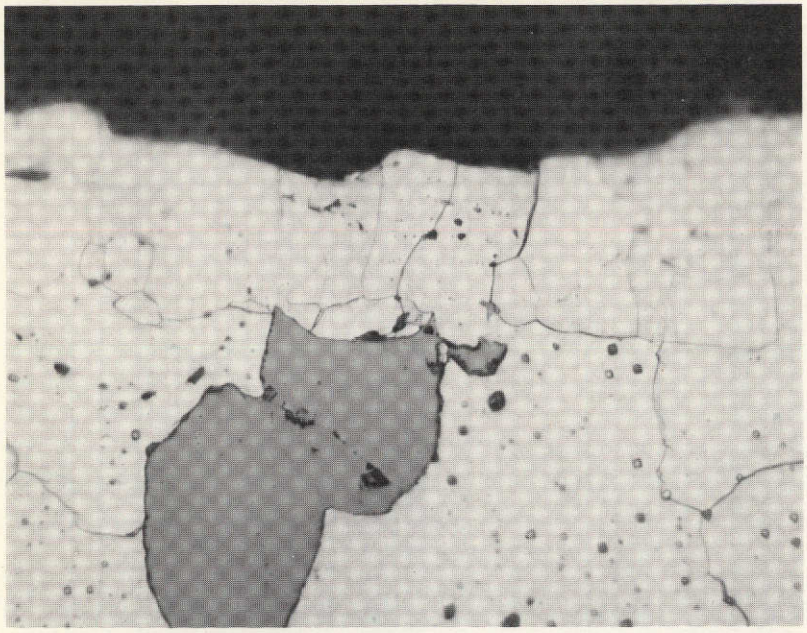
OPERATING CONDITIONS FOR SG-1 PLASMA GENERATOR DURING PREPARATION OF EDGE-COATED SAMPLES TESTED AT NASA

Run Number	Running Time on Front Electrode*, min.	Operating Voltage†, v.	Current, amp.	Power, kw.	Torch-To-Work Distance, in.	Gas Flows, l./min.		
						Helium Arc Gas	Hydrogen Cover Gas	Helium Powder Gas
5-C-1	325	50	480	24.0	2	69	7.20	1.44
5-C-2	388	50	480	24.0	2	69	7.20	1.44
5-C-3	350	50	480	24.0	2	69	7.20	1.44
5-C-4	363	49	490	24.0	2	69	7.15	1.44

* For these tests, electrodes normally used for argon were used with helium as shown. This arrangement was determined empirically but was later recommended by the manufacturer.

† Open circuit voltage, 160 volts dc.

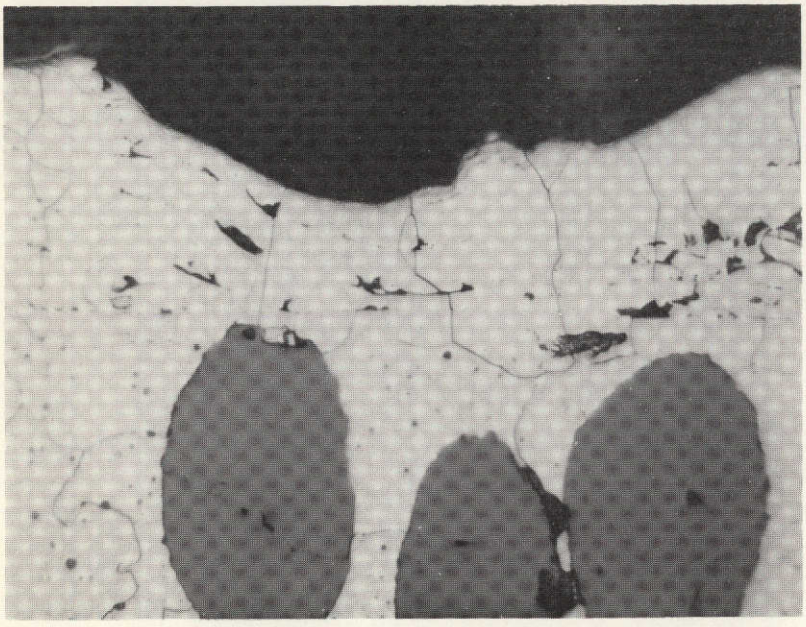
‡ Edge clad using minus 325 plus 400-mesh tungsten spray powder; the other samples were clad using minus 230 plus 325-mesh tungsten spray powder.



Sample 1-C-1

Core Clad Interface

Side 1



Sample 1-C-6

Core Clad Interface

Side 1

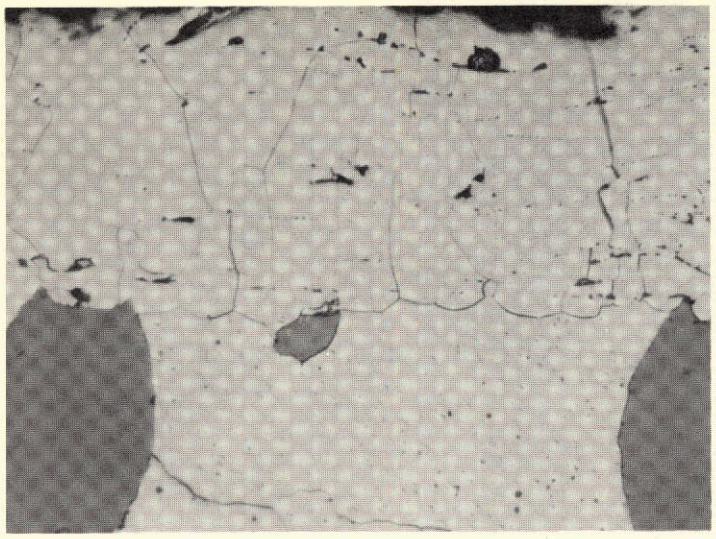
Magnification - 500 X
(Etchant - Murakami's Reagent)

Distance - 1-3/4 inches

Speed - 30 in./min.

CROSS-SECTION OF PLASMA-SPRAYED FUEL PLATE (Set 1)

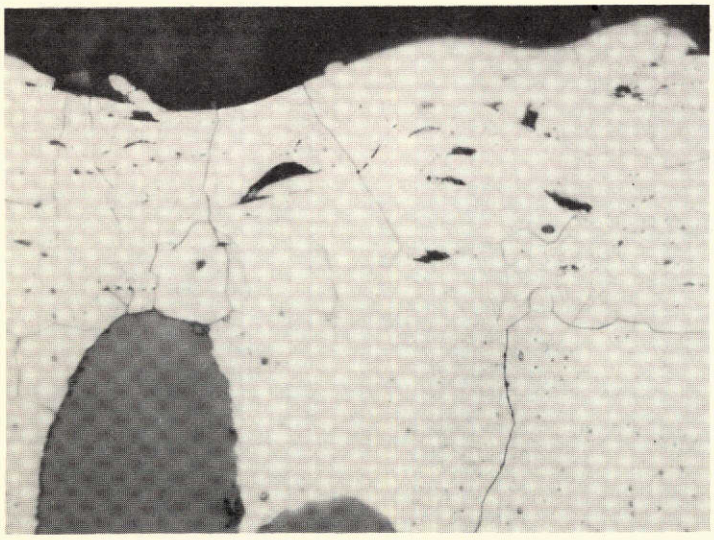
Figure 2



Sample 2-C-1

Core Clad Interface

Side 4



Sample 2-C-6

Core Clad Interface

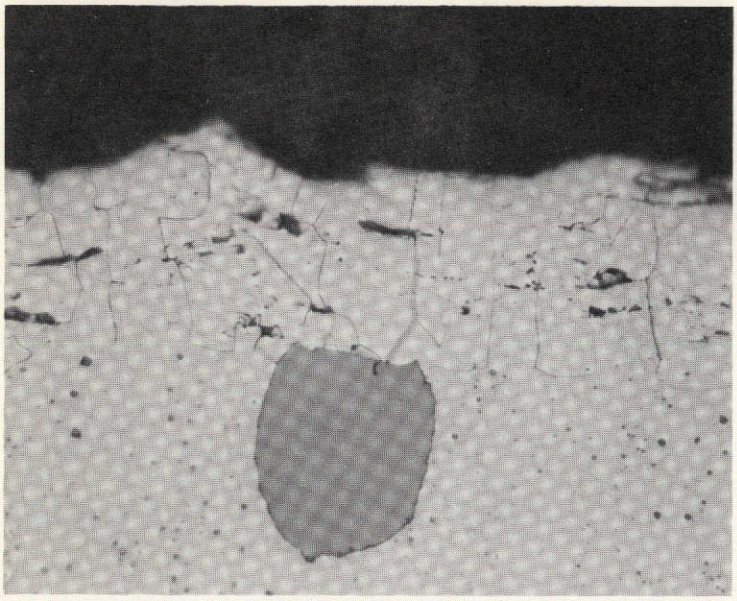
Side 2

Magnification - 500 X
(Etchant - Murakami's Reagent)

Distance - 1-7/8 inches Speed - 30 in./min.

CROSS-SECTION OF PLASMA-SPRAYED FUEL PLATE (Set 2)

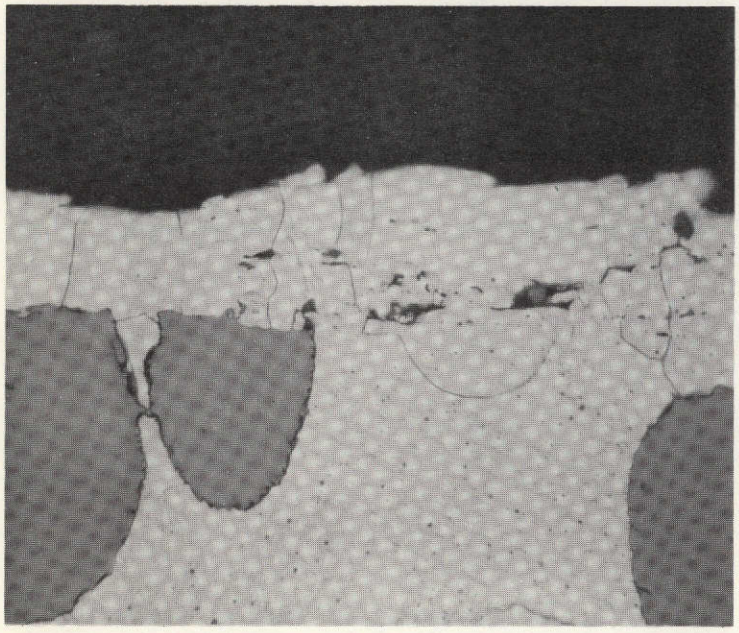
Figure 3



Sample 3-C-5

Core Clad Interface

Side 1



Sample 3-C-5

Core Clad Interface

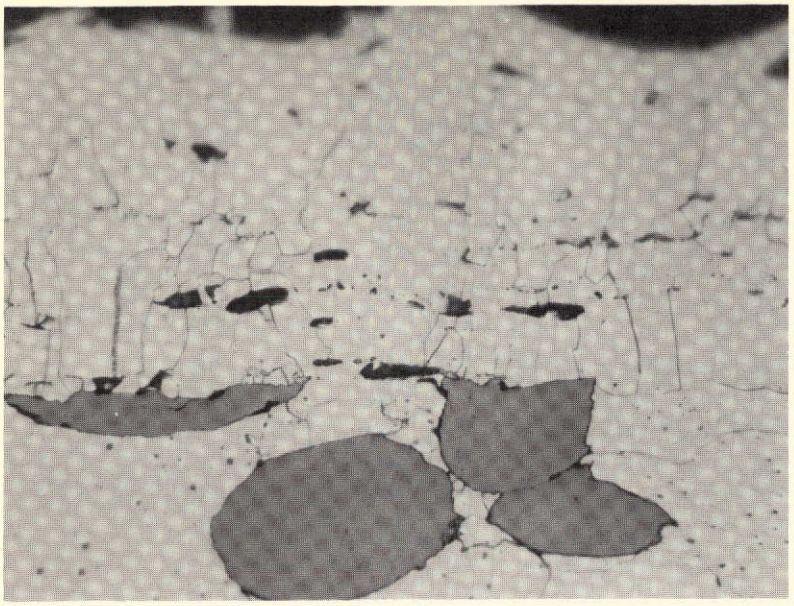
Side 2

Magnification - 500 X
(Etchant - Murakami's Reagent)

Distance - 2 inches Speed - 30 in./min.

CROSS-SECTION OF PLASMA-SPRAYED FUEL PLATE (Set 3)

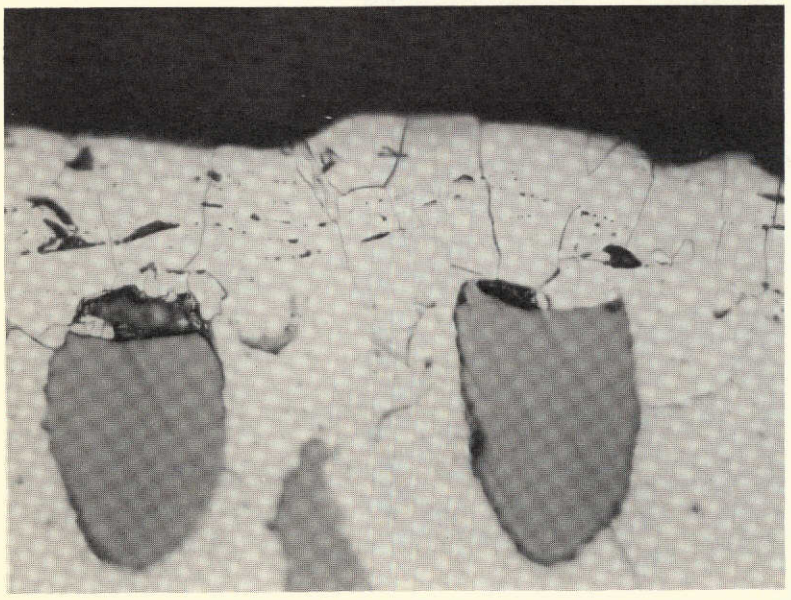
Figure 4



Sample 4-C-5

Core Clad Interface

Side 1



Sample 4-C-5

Core Clad Interface

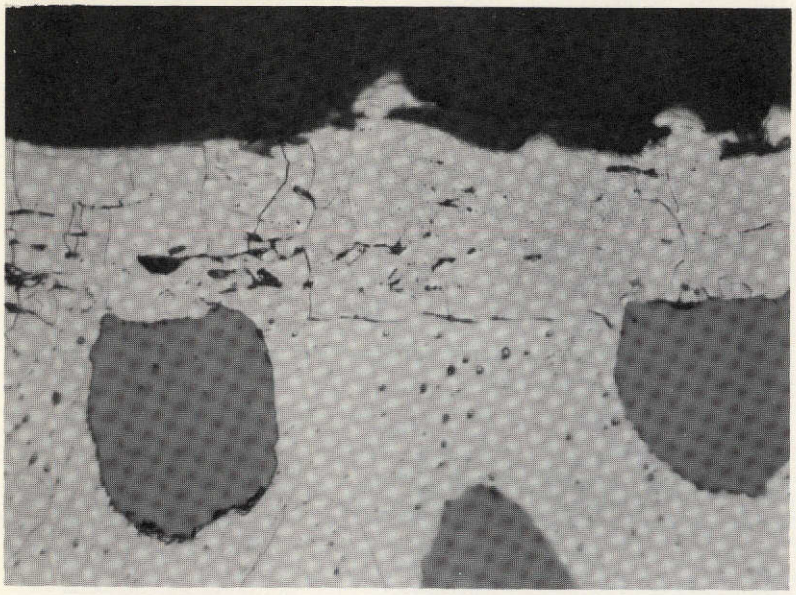
Side 2

Magnification - 500 X
(Etchant - Murakami's Reagent)

Distance - 2 inches Speed - 30 in./min.

CROSS-SECTION OF PLASMA-SPRAYED FUEL PLATE (Set 4)

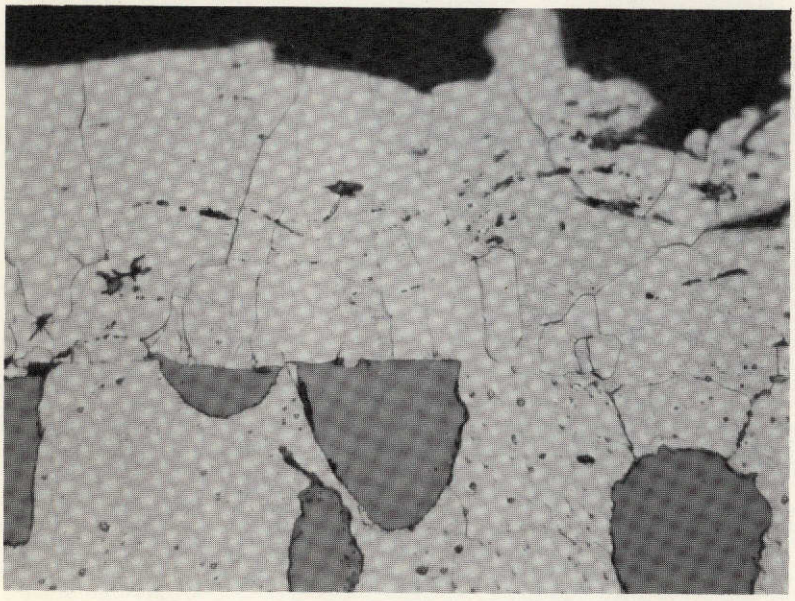
Figure 5



Sample 5-C-5

Core Clad Interface

Side 2



Sample 5-C-5

Core Clad Interface

Side 4

Magnification - 500 X
(Etchant - Murakami's Reagent)

Distance - 2 inches

Speed - 30 in./min.

CROSS-SECTION OF PLASMA-SPRAYED FUEL PLATE (Set 5)

Figure 6

It should be pointed out that good fuel retention was obtained on samples which were coated at torch-to-work distances varying from 1-3/4 inches to 2 inches and with two different sizes of tungsten spray powders. In general, these data show that the process was under control and that the plasma spraying produced coatings which reduce uranium dioxide loss when the coated specimen is operated at elevated temperatures.

TABLE III

EFFECT OF PLASMA-SPRAYED TUNGSTEN EDGE COATING ON URANIUM DIOXIDE FUEL RETENTION DURING 2-HOUR, 2485°C. STATIC TESTING IN FLOWING HYDROGEN (35 std. cfh.)
(NASA Data)

Sample Number	Fuel Loss, weight percent
Unclad Sample (Control)	3
1-C-3	0.33
1-C-4	0.51
3-C-3*	0.31
3-C-4*	0.38
4-C-3	0.25
4-C-4	0.11
5-C-3	0.32
5-C-4	0.45

* Edge-clad using minus 325 plus 400-mesh tungsten spray powder; others clad using minus 230 plus 325-mesh tungsten spray powder.

Additional Improvements to the Edge Coating System

Since these samples were prepared, some additional improvements have been made to the system to ensure day-to-day replication. These changes have included the installation of an automatic valve sequence program which should result in a uniform gas composition from run to run within the controlled atmosphere chamber. An oxygen analyzer and moisture analyzer have also been installed to monitor automatically the chamber gas purity and the purity of the helium gas fed to the torch and powder feeders. Preliminary data with this system indicate that, although the oxygen content drops to a very low level shortly after the plasma torch begins operation, there is an attendant increase in moisture content. Additional experience is needed to determine the magnitude and severity of this problem. For some time, an oscilloscope has been used to monitor periodically the voltage and the current used in the plasma generator on the assumption that the electrode surface condition would influence the instantaneous current and voltage wave forms and that, as

changes would occur to the conducting surfaces, the wave form would also change. It is not possible at this time to draw definite conclusions, but it is believed that this will begin to generate meaningful information as more experience is gained.

Cladding Flat Fuel Elements

While the environmental tests were being run at NASA on the initial nine edge-coated samples, two scoping tests were performed to determine the problems involved in plasma coating the entire surfaces of flat cermet fuel elements. In both of these tests, spray conditions used previously with the SG-3 plasma generator in the edge coating work were employed. At these conditions, excessive warping of the substrate occurred because of the large temperature gradient which existed during coating. From the results of these tests, it is apparent that special precautions will be needed to avoid warping. A combination of special jigging and preheating might be effective. Further work in this area was deferred to concentrate the effort on edge coating.

JOINING STUDIES

The work on joining tungsten-uranium dioxide cermets with plasma spraying has been limited to two areas: (a) the development of a fueled joint produced by the codeposition of tungsten and uranium dioxide, and (b) the formation of a T-joint with plasma-sprayed tungsten. Only a few scoping studies had been completed in either area before the emphasis was switched to edge coating.

Codeposition of Tungsten and Uranium Dioxide by Plasma Spraying

Unfueled joints or welds in the nuclear powered rocket engine could be detrimental from the nuclear standpoint; thus, a technique which could be used to produce a fueled joint, either for patching, for welding concentric tube fuel elements, or even for fuel element fabrication would be desirable. In the first series of five exploratory tests, no effort was made to produce a fueled joint. Instead, a mixture of tungsten and uranium dioxide was plasma-sprayed onto a tungsten substrate, and the characteristics of the deposit was examined microscopically to determine the potential of this technique.

In four of the tests, micronized uranium dioxide generated as a by-product of the uranium dioxide spheroidization process was co-sprayed with minus 270 plus 325-mesh tungsten powder. In the first two attempts, both powders were blended, and the mixture was plasma sprayed. Poor bonding of the tungsten particles occurred due to excessive torch-to-substrate distance in the first attempt, and the tungsten and uranium dioxide mixture melted on the second sample. The melting resulted in streaks of uranium dioxide in the tungsten grain boundaries.

In the second pair of runs, the tungsten and the uranium dioxide powders were introduced into the plasma stream at different locations in an effort

to obtain sufficient heating of the tungsten while avoiding overheating of the uranium dioxide. These two tests were conducted using normal spray tungsten and the SG-1 plasma generator. The position of the second feed point was changed so that the uranium dioxide would reach a different temperature in each case. A photomicrograph of a cross-section of one of these samples appears in figure 7. The method shows considerable promise in that a fully dense tungsten matrix was formed; however, the uranium dioxide had once again reached the molten state and had diffused along the tungsten grain boundaries. Apparently, there was enough latent heat available in the tungsten particles when heated to the plastic state to melt the uranium dioxide particles. Subsequent tentative calculations indicate that a uranium dioxide loading of as much as 40% may be required to prevent the heat from the molten tungsten droplets from being great enough to cause uranium dioxide melting.

One other attempt was made to codeposit tungsten and uranium dioxide by plasma spraying. For this test, tungsten-coated uranium dioxide which had been prepared in the fluidized bed was used as the spray powder. The spraying attempt resulted in catastrophic decoating of the individual powder particles. It appeared that each particle ruptured with explosive force. The tungsten settled in one area of the spray chamber, the uranium dioxide settled in another, and there was no deposit on the substrate. It is believed that the coating disintegration can be attributed to the high fluoride content of the particular powder used in this test and that better results may be obtained with higher purity coated powders.

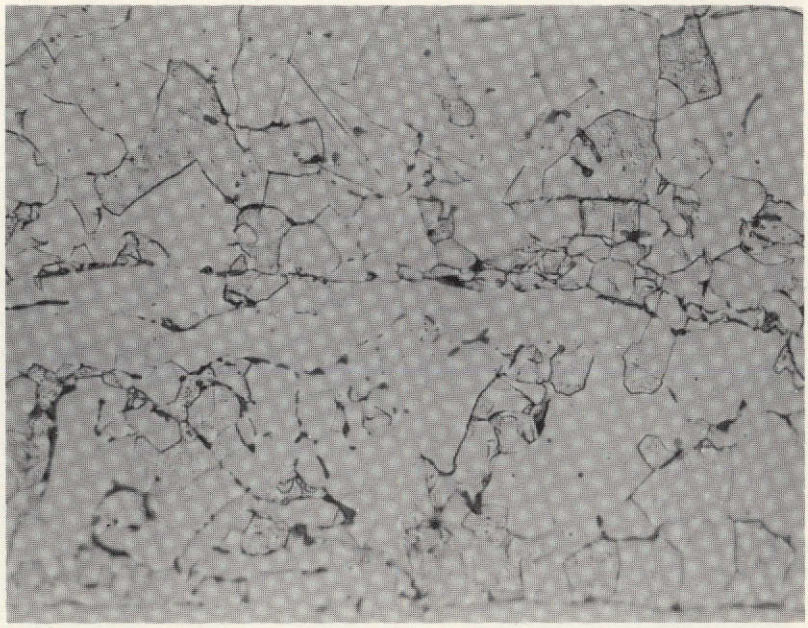
After the above tests, work in this area was held in abeyance due to emphasis on edge coating.

Formation of Tungsten T-Joints

Two brief attempts were made to form a T-joint between two tungsten strips by plasma spraying. The use of spray conditions developed for edge coating resulted in the formation of a joint; however, the results made it clear that a considerable amount of development work would be needed to produce an acceptable process. Excessive amounts of tungsten were applied at the joints in the areas where there was a good fit between the surfaces, but no joining took place at the areas of poor fit. Jigging and alignment of the pieces to be joined will require considerable development effort, and additional work will be needed to determine the spraying conditions that will control the width of the joint.

CONCLUSIONS

During the course of this development program, procedures and operating conditions were established by which fully dense, metallurgically bonded, tungsten coatings could be plasma sprayed on the edges of tungsten-uranium dioxide cermet, flat-plate, fuel elements without melting the uranium dioxide. Using helium arc gas, the SG-1 plasma gun operated at a power level of 24 kw. in a recirculating helium-10% hydrogen atmosphere appeared to be the most effective system from the standpoints of acceptable



Magnification - 1000X

TUNGSTEN-URANIUM DIOXIDE MATRIX
CODEPOSITED BY PLASMA SPRAYING
(Etchant - Murakami's Reagent)

Figure 7

equipment life, coating quality, versatility, and reproducibility. Edge coating, 3 to 4 mils thick, were applied at a traverse speed of 30 inches per minute and at torch-to-work distances varying from 1-3/4 to 2 inches. These coatings were effective in reducing uranium dioxide loss from the fuel plates when they were subjected to high temperature tests at the NASA Lewis Research Center.

The exploratory studies on (a) coating the flat surface of cermet fuel elements, (b) forming T-joints, and (c) forming fueled joints by codeposition of tungsten and uranium dioxide were too limited to define the required spraying conditions; however, based on the experience gained in the edge coating program, it appears that a plasma spray system could be developed for successfully accomplishing these operations.

ACKNOWLEDGEMENTS

The authors are indebted to S. H. Smiley and W. E. Tewes for suggestions and advice and for guidance in the management of the technical programs. The authors are also grateful to R. M. Caves of the NASA Lewis Research Center for permission to present the results of his thermal cycling test on edge-coated fuel elements. Acknowledgement is made to the Works Laboratory for performance of the various analyses used in this report.

BIBLIOGRAPHY

(1) Grisaffe, S. J., and Caves, R. M., Fuel Retention Improvement at High Temperatures in Tungsten-Uranium Dioxide Dispersion Fuel Elements by Plasma-Spray Cladding, NASA Lewis Research Center, November, 1964 (NASA TM-X-1028).

(2) Gedwill, M. A., Sikora, P. R., and Caves, R. M., Fuel Retention Properties of Tungsten-Uranium Dioxide Composites, NASA Lewis Research Center, February, 1965 (NASA TM-X-1059).

NOTEBOOK REFERENCES

1. Knight, R. G., ORGDP Research Notebook Number 4865.

2. Stanley, F. S., ORGDP Research Notebook Number 4677.

PART III

TUNGSTEN COATING OF URANIUM DIOXIDE PARTICLES

By

W. L. Cochran
R. G. Knight
F. S. Stanley

Engineering Development Department
Technical Division

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

(Identification C-25101A)

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Materials and Structures Division
Robert M. Caves

Part III: TUNGSTEN COATING OF URANIUM DIOXIDE PARTICLES

SUMMARY

The objective of this project was to develop a new method for producing a 3- to 5-micron thick, pure, dense, tungsten coating on 30- to 60-micron uranium dioxide powder. The approach to this problem was the development of new techniques for depositing a thin, protective tungsten coating on the powder which could then be built up to the desired thickness by a conventional gas plating process. The purpose of the thin, protective coating was to prevent fluoride formation caused by hydrogen fluoride attack of the unprotected uranium dioxide during gas plating.

Scoping studies have been run on four new coating techniques: (a) electrostatic bonding, plasma jet coalescence; (b) electrostatic bonding, fluid-bed sintering; (c) electrostatic bonding, static bed sintering; and (d) vacuum evaporation in an electron beam apparatus. The results of the first approach were discouraging. Uranium dioxide particles were coated successfully with fine tungsten powder or with fine tungsten trioxide by the electrostatic technique, but when the coated particles were processed through the plasma jet, the coating melted into spheroids instead of forming a uniform layer on the surface of the uranium dioxide particles. A partially protective film was deposited by the electrostatic bonding, fluid-bed sintering method. This film produced a significant reduction in the fluoride content of a tungsten coating subsequently deposited by the hydrogen reduction of tungsten hexafluoride. The coating produced by the electrostatic bonding, static-bed sintering technique was non-protective.

In the final approach, a partially protective film was deposited by vacuum evaporation in an electron beam apparatus.

INTRODUCTION

The objective of this task was to perform scoping studies on several methods for depositing a tungsten coating on 30- to 60-micron uranium dioxide powder for use in connection with materials research for the tungsten-184 water-moderated nuclear rocket concept under study at the NASA Lewis Research Center[1]. The desired end product was a 3- to 5-micron coating of tungsten on each uranium dioxide particle applied so as to be pure, dense, and crack-free. The cladding should maintain its integrity and should retain the uranium dioxide up to temperatures of at least 2500°C. The cladding would also assure uniform dispersion of the uranium dioxide in the tungsten-uranium dioxide cermet fuel elements and would eliminate any interconnection between uranium dioxide particles. Total metallic impurities should be less than 50 ppm., and the halide content should be less than 15 ppm. Representative samples of the coated particles were to be submitted to NASA for testing and evaluation.

The work statement for this program outlined three methods which might be utilized: (a) plasma coating by evaporation-condensation; (b) electrostatic bonding, plasma jet coalescence; and (c) electrostatic bonding, fluid-bed sintering. The latter technique was eventually extended to include static-bed sintering. One other approach which has shown considerable promise is that of vapor deposition utilizing an electron beam system. The plan is to deposit a thin, protective layer of tungsten and then to use gas plating to obtain the desired thickness. If protective, the thin layer would prevent formation of fluorides during the subsequent gas plating operation. Thus, fluoride contamination during gas plating was used to determine the protection afforded by the thin layer of tungsten.

PLASMA COATING BY EVAPORATION-CONDENSATION

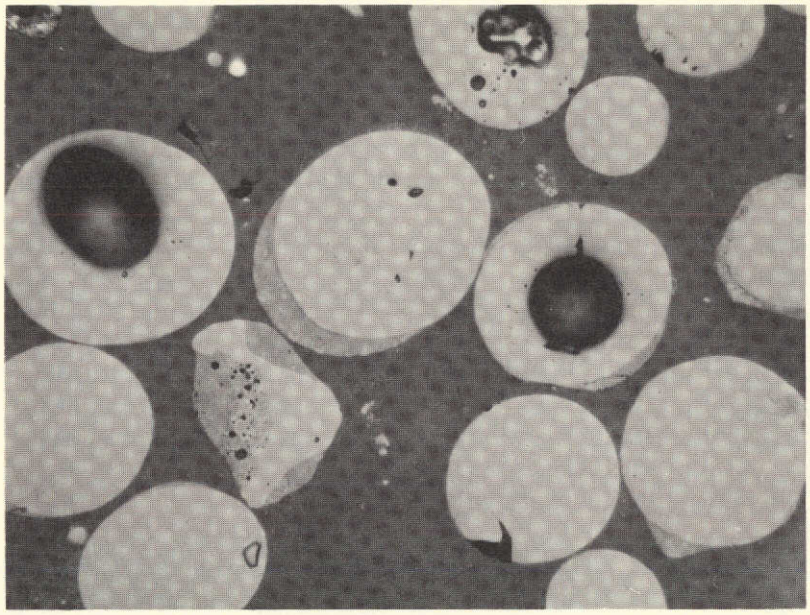
No direct effort has been placed upon this approach due to the emphasis in other areas of this activity.

ELECTROSTATIC BONDING, PLASMA JET COALESCENCE

Several scoping studies were conducted. In these experiments, finely divided tungsten powder produced by the ORGDP flame reduction process or fine tungsten trioxide was mixed with partially spheroidized 30- to 150-micron uranium dioxide powder in a tungsten rod mill to cause the tungsten or tungsten trioxide particles to adhere to the uranium dioxide particles. In the first test, tungsten powder was blended with uranium dioxide; then, the mixture was fed at about 19 grams per minute to the SG-1 plasma system operating at 30 kw. with a mixture of 90% helium and 10% hydrogen as the arc gas. When the plasma jet product was sectioned and was examined metallographically, it was found that the tungsten particles had melted but had not coated the uranium dioxide powder. There was some adherence of the tungsten to the uranium dioxide substrate, usually as a smaller spheroidal tungsten particle on the surface of a larger uranium dioxide particle. In some cases, the uranium dioxide had encapsulated the tungsten, indicating that a number of uranium dioxide particles had melted in the plasma jet.

In the other tests, tungsten trioxide powder was used instead of metallic tungsten powder. It was anticipated that it might be possible either to melt the tungsten trioxide and to reduce it to tungsten without melting the uranium dioxide or to form a coating of tungsten trioxide on the particles which subsequently could be reduced to tungsten in a fluidized bed.

In one of these tests, the mixture of tungsten trioxide-uranium dioxide was fed to the SG-1 90% helium-10% hydrogen plasma system, and the resultant powder was clean and free of coating. It appeared that the tungsten trioxide was vaporized while passing through the plasma jet. To minimize the vaporization and to prevent reduction of the tungsten trioxide to tungsten, a low energy argon plasma was utilized for the other test. In figure 1, it can be seen that some coating did take place. This coating



Sample J-5 Magnification - 500 X

TUNGSTEN TRIOXIDE ON URANIUM DIOXIDE
SINTERED IN AN ARGON PLASMA
(CrO_3 Attack Polish)

Figure 1

is tungsten trioxide, and it should be possible to convert it to tungsten metal without difficulty in the fluidized bed. It should be noted, however, that the coating is not uniform. It is possible that improved blending techniques may increase the uniformity. Subsequent coating of this material by conventional gas plating techniques was not attempted.

ELECTROSTATIC BONDING, FLUID-BED SINTERING

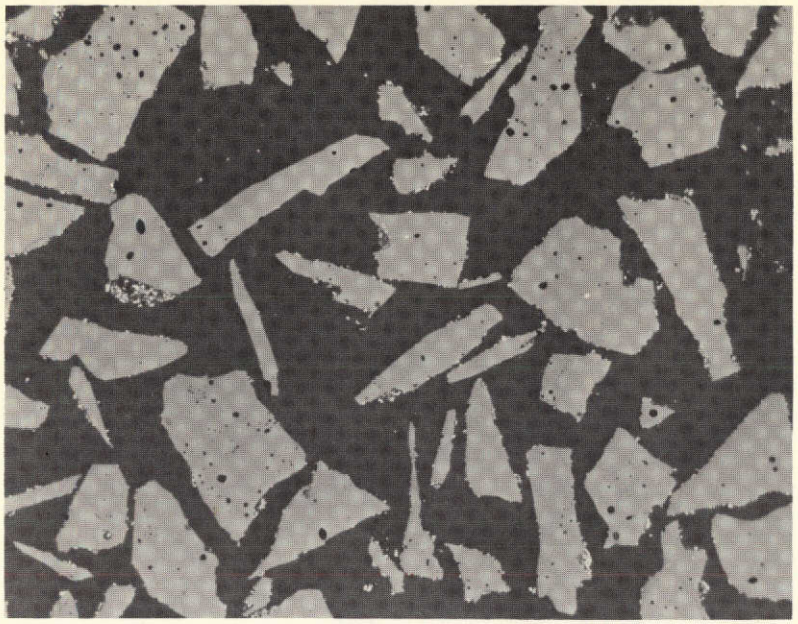
The original plans called for electrostatically coating 30- to 60-micron uranium dioxide particles with a layer of fine tungsten powder which would then be sintered in a fluidized bed to produce a dense, impervious coating. The experience with the plasma coating indicated that it would be difficult to attain complete densification of the tungsten without melting the uranium dioxide; therefore, the same general technique was used, but tungsten trioxide was employed as the coating material. The fine tungsten trioxide was blended with 30- to 60-micron uranium dioxide powder and was reduced to the metal with hydrogen at 870°C. in a fluidized bed. After gas plating with tungsten to a thickness of 5 microns, the powder had a fluoride content of 1,300 ppm. If extrapolated to an 8-micron tungsten coating, the fluoride content would be reduced to about 700 ppm.; i.e., a reduction of about one-third compared with gas plating alone (i.e., approximately 1000 ppm). The fluoride content of the coated particle will depend upon the thickness of the tungsten coating because thicker coatings will dilute the fluoride percentage in the powder. To place all results on a common basis, fluoride values are calculated for each sample for a 8-micron coating.

In another run, uranium dioxide was blended with tungsten trioxide, reduced, blended again with additional tungsten trioxide, reduced a second time, and then coated with about 4 microns of tungsten by conventional gas plating. The resultant fluoride content, 900 ppm. or about 450 ppm. for an 8-micron coating, was very encouraging; however, this technique may leave something to be desired, since the sectioned samples, figure 2, indicate that the bonding of the coating to the powder particle may be less than that achieved with either straight gas plating or vacuum deposition followed by gas plating.

Since some of the tungsten trioxide coating may have been removed by the abrasive action of the fluid bed, an additional coating test was conducted where the tungsten trioxide was reduced in a static bed. The resultant mixture was sectioned for examination and is shown in figure 3. This powder was subsequently coated with about 4 microns of tungsten by gas plating. The fluoride content of 2,500 ppm., equivalent to about 1,000 ppm. when plated to 8 microns, was in the range usually experienced with gas plating alone.

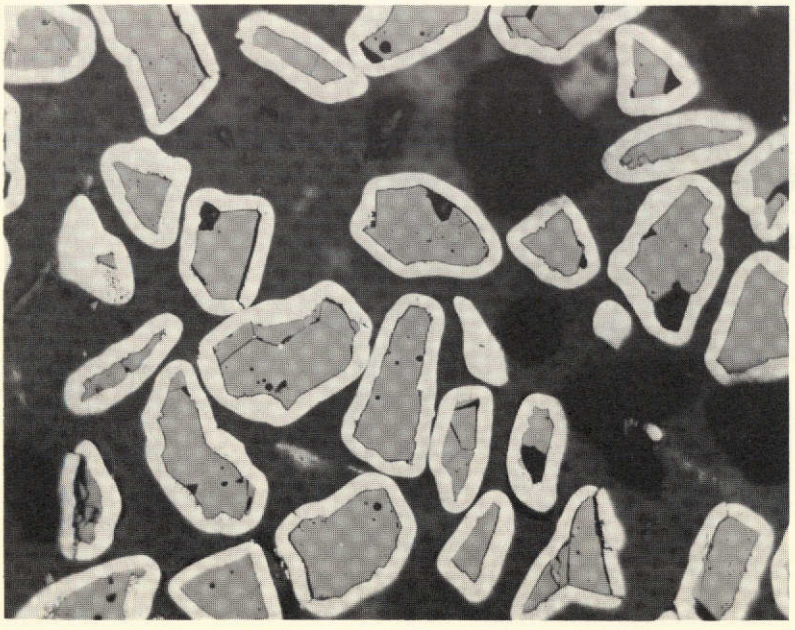
VAPOR DEPOSITION OF TUNGSTEN UTILIZING THE ELECTRON BEAM SYSTEM

Encouraging results have been obtained on the development of a method for the deposition of tungsten on powder particles by vacuum evaporation



Sample K-218 Magnification - 250 X

Electrostatically Coated with Tungsten Trioxide,
Reduced and Sintered in a Fluid Bed

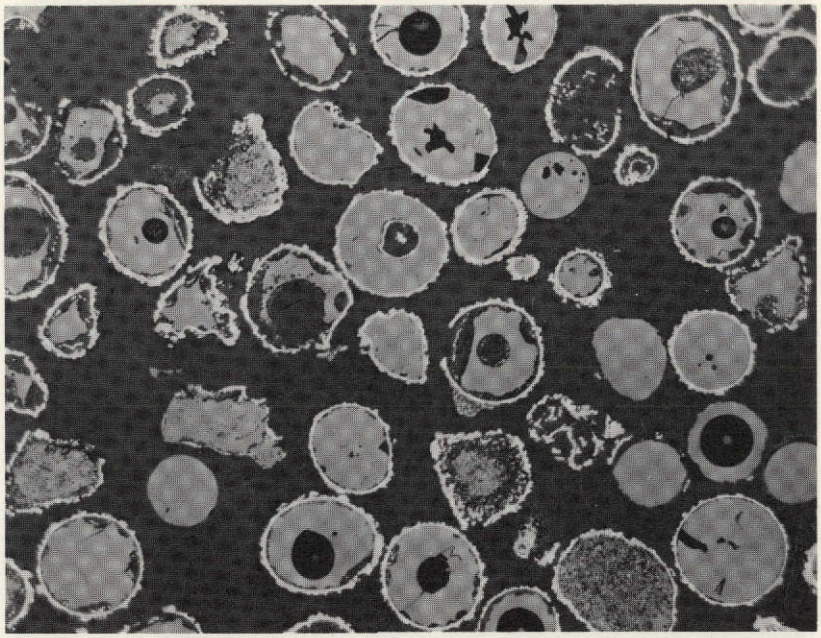


Run WF-279 Magnification - 250 X
Sample K-219

After Vapor Coating by the
Hydrogen Reduction of Tungsten Hexafluoride

TUNGSTEN-COATED 30- TO 60-MICRON URANIUM DIOXIDE
(CrO_3 Attack Polish)

Figure 2



Sample K-265 Magnification - 250 X

URANIUM DIOXIDE ELECTROSTATICALLY COATED WITH TUNGSTEN TRIOXIDE, THEN REDUCED AND SINTERED IN A STATIC BED (CrO_3 Attack Polish)

Figure 3

in an electron beam apparatus. A 9 kw. electron beam welding machine with the gun mounted in the horizontal position was used to perform the experiments. As shown in figures 4 and 5, the uranium dioxide powder was placed inside the 6-1/2-inch diameter canister with a hole at each end, and this unit was rotated by a liquid nitrogen-cooled drum roller mounted in the 2-foot by 2-foot by 2-foot vacuum chamber of the electron beam apparatus. The beam of electrons entered through a hole in one end of the canister and was focused onto the end of a tungsten rod which protruded through a hole in the other end of the canister. Tungsten, vaporized from the end of the rod by heat caused by electron bombardment, condensed on the powder particles which were raised and tumbled by the lifting flights attached to the interior of the rotating canister.

In performing these experiments, the following general observations can be made regarding equipment performance.

Electron Beam Apparatus

While this coating technique required rather long periods of sustained operation at high power levels, the electron beam welder is designed for relatively short periods of continuous operation. The excessive heat generated by the filament was not easily dissipated and caused frequent filament burnout and shortened the life of other gun components. Most of these problems were eliminated by redesign of the component parts.

Beam Stability

The beam of electrons can be deflected by the charge which rapidly builds up on ceramic powder. Canister redesign and minor modifications to the operating procedure minimized this tendency but did not eliminate it completely.

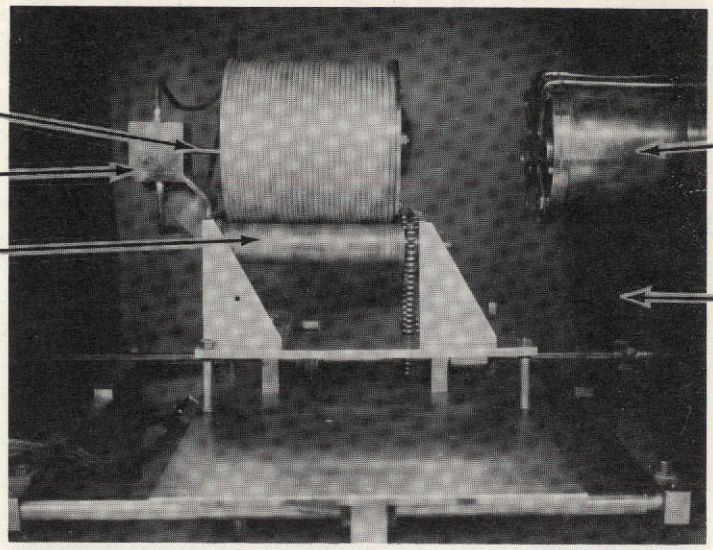
Mechanical

Vaporizing tungsten for extended periods of time released a relatively large amount of heat. Efforts to cool the drum roller and canister during operation were only partly successful, and the roller mechanism frequently failed during the early tests. The range of temperatures between liquid nitrogen and molten tungsten caused failure of seals and fittings and resulted in frequent shutdowns because of loss of vacuum.

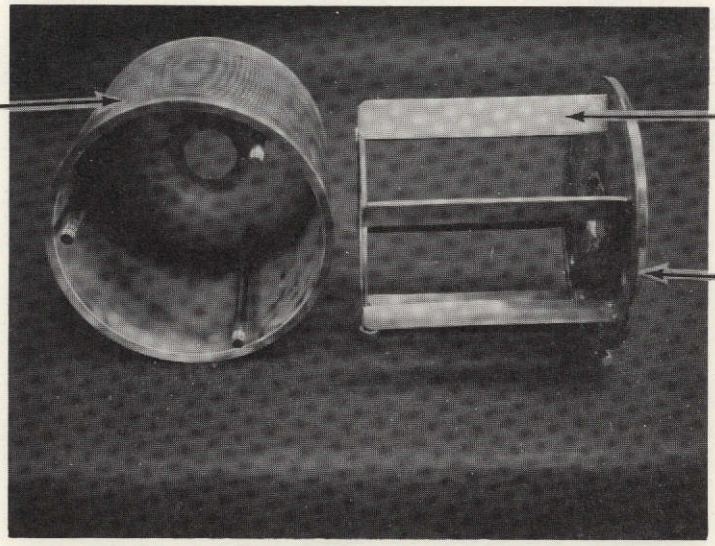
Product Contamination and Material Loss

When uranium dioxide particles were struck by the beam, instant vaporization occurred. The vaporized uranium dioxide was either lost or deposited onto the powder being coated. The latter case resulted in contamination in the coating, and the best operating conditions and canister design did not eliminate this problem completely, although considerable improvement was achieved.

In the initial test with 60-mesh alumina, the powder appeared to be coated completely. Alumina was selected for the first test to make the tungsten readily visible.



Assembly

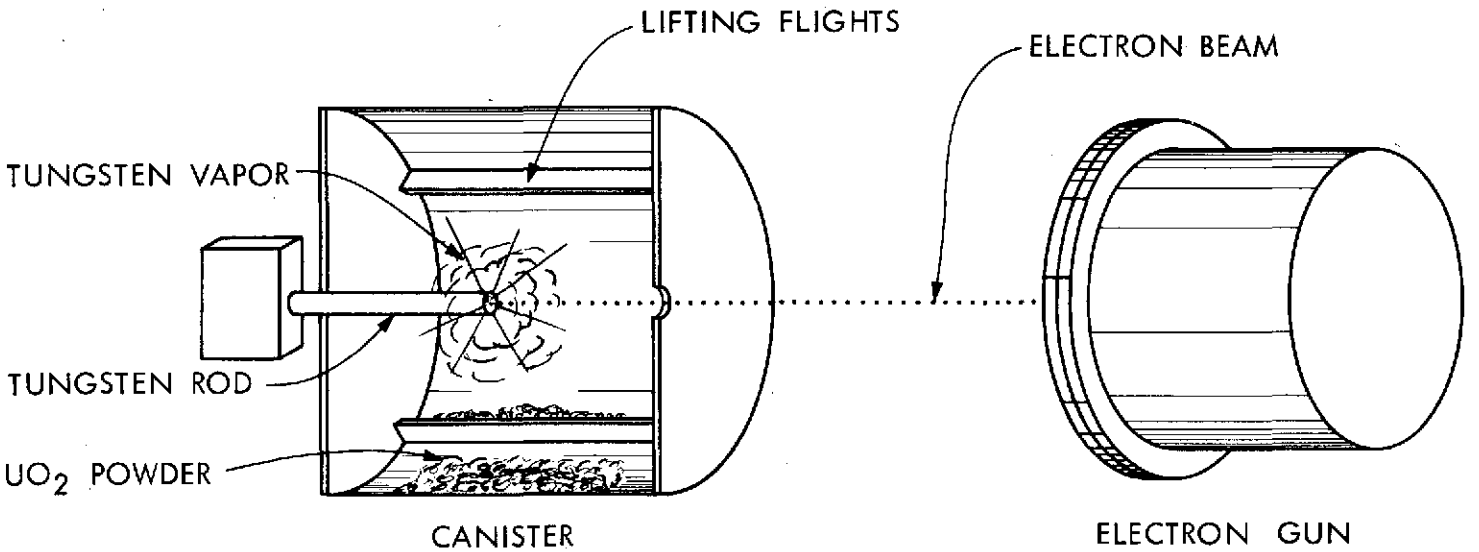


Canister

ELECTRON BEAM APPARATUS USED FOR
TUNGSTEN COATING URANIUM DIOXIDE PARTICLES
BY VACUUM EVAPORATION

Figure 4

DWG. NO. G-65-480



ELECTRON BEAM TUNGSTEN COATING SYSTEM

Figure 5

One sample of uranium dioxide powder which had been in the coating system for 1-1/2 hours was sectioned and examined. Some of the sectioned particles appeared to be coated completely with a layer of tungsten about 2,000 angstroms thick. Other particles in the same field of view appeared to be only partly coated or bare. When this same powder was observed at low magnification prior to cross-sectioning, about 80% of the particles appeared to be coated completely. It is possible that many of the particles which seemed to be coated prior to sectioning appeared to be uncoated in cross-section because the coating thickness was below the limit of resolution of the microscope.

In the first test on material which was tungsten-coated by vacuum evaporation and was then gas-plated with about 5 microns of tungsten, figure 6, the fluoride content is 1,700 ppm., which is equivalent to about 800 ppm. for the standard 8-micron coating thickness. While this is only about three-fourths the fluoride value for conventional gas plating, it is still much higher than is desired.

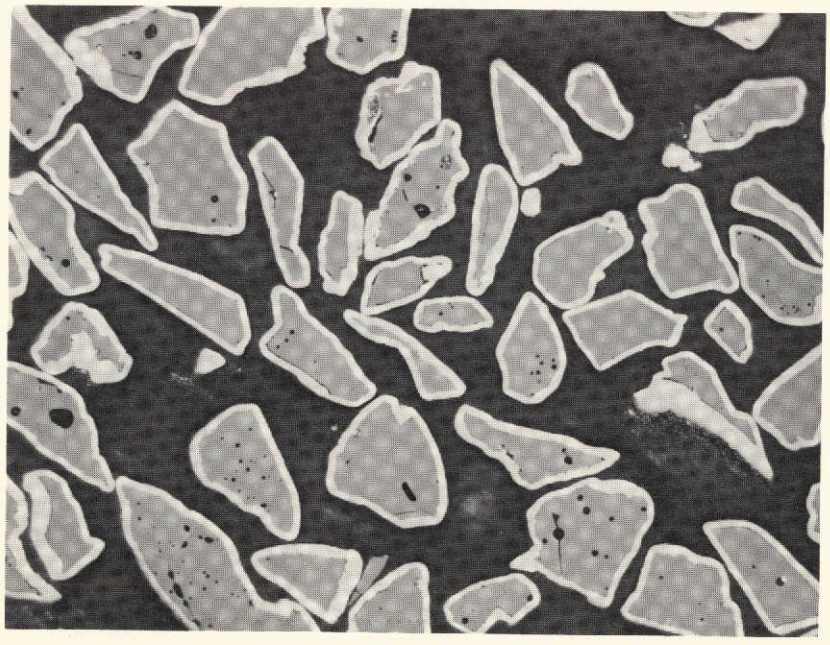
An additional 160-gram batch of uranium dioxide powder was run for a total of 1-1/2 hours in the electron beam coating apparatus and was then coated with an estimated 3.7 microns of tungsten by conventional gas plating techniques. The resultant fluoride content of 1,000 ppm. is equivalent to about 500 ppm. should the full 8-micron thick tungsten coating be applied. This is slightly less than one-half the normal value of a sample coated by gas plating alone. Additional tests are required to determine if the deposition of a thicker film by the electron beam process will provide improved protection and lower fluoride content in the gas-plated powder; however, the program terminated before these tests could be completed. It is a point of interest that the electron beam technology is suitable for a wide variety of coating materials.

CONCLUSIONS

The scoping studies made in the performance of this task demonstrated the feasibility of two promising methods for depositing a thin coating of tungsten on 30- to 60-micron uranium dioxide particles; however, further development of these methods is required. The coatings showing most promise were produced by vacuum evaporation using an electron beam for a heat source to evaporate the tungsten and by electrostatically bonding fine tungsten oxide powder onto the uranium dioxide and then reducing the coating to tungsten in either a fluid or a static bed. Although none of the thin tungsten coatings applied by the various methods were completely effective in eliminating halide contamination when the powders were subsequently gas plated, it is felt that both the electron beam evaporation and the electrostatic bonding techniques could be developed into workable processes. The techniques developed in this program also should be applicable to the deposition of thin films of a wide variety of materials onto selected substrates.

Sample K-224 Magnification - 500 X

Uranium Dioxide Coated with Tungsten
in the Electron Beam Apparatus



Run WF-281
Sample K-232 Magnification - 250 X

Same Powder as Above after Tungsten Coating by the
Hydrogen Reduction of Tungsten Hexafluoride

TUNGSTEN COATED URANIUM DIOXIDE
(CrO_3 Attack Polish)

Figure 6

ACKNOWLEDGEMENTS

The authors are indebted to S. H. Smiley and W. E. Tewes for suggestions and advice and for guidance in the management of the technical programs. Acknowledgement is made to the Works Laboratory for performance of the various analyses used in this report.

BIBLIOGRAPHY

(1) Gedwill, M. A., Sikora, P. F., and Caves, R. M., Fuel Retention Properties of Tungsten-Uranium Dioxide Composites, NASA Lewis Research Center, February, 1965 (NASA TM-X-1059).

NOTEBOOK REFERENCES

1. Cochran, W. L., ORGDP Research Notebook Number 4854.

2. Knight, R. G., ORGDP Research Notebook Number 4895.

3. Stanley, F. S., ORGDP Research Notebook Number 4804.

DISTRIBUTION

OAK RIDGE GASEOUS DIFFUSION PLANT

Standard Internal (26 copies)

SPECIAL

Argonne National Laboratory, Argonne, Illinois: J. Schumar, R. Noland (2)
Atomic Energy Commission, Washington, D. C., Division of Reactor Development: S. Christopher
Atomic Energy Commission, Washington, D. C.: Library (3)
Atomic Energy Commission, Oak Ridge, Tenn., Division of Technical Information Extension (3)
Atomics International, Canoga Park, Calif.: S. Carneglia
Battelle Memorial Institute, Columbus, Ohio: E. Hodge
General Electric Company, Vallecitos Atomics Laboratory, Pleasanton, Calif.: A. Kaznoff
General Electric Company, Evandale, Ohio: J. McGurty
General Atomics Division, San Diego, Calif.: A. Weinberg
Jet Propulsion Laboratory, Pasadena, Calif.: Library
Martin-Marietta Corporation, Baltimore, Md.: W. McDaniels
Minnesota Mining and Manufacturing Company, St. Paul, Minn.: J. Ryan
NASA Ames Research Center, Moffett Field, Calif.: Library
NASA Flight Research Center, Edwards, Calif.: Library
NASA Goddard Space Flight Center, Greenbelt, Md.: Library
NASA Langley Research Center, Hampton, Va.: Library
NASA Lewis Research Center, Cleveland, Ohio:

Caves, R. M.	Saunders, N. T. (3)
Creagh, J.	Smreker, H.
Fackler, J. J.	Library (2)
Gluyas, R. E.	Nuclear Rocket Technology Office
Kaufman, S.	Office of Reliability and Quality Assurance
Moss, T.	Report Control Office
Musial, N. T.	Technical Utilization Office

NASA Manned Spacecraft Center, Houston, Texas: Library
NASA Marshall Space Flight Center, Huntsville, Ala.: Library
NASA Scientific and Technical Information Facility, Bethesda, Md.: (6)
NASA Western Operations, Santa Monica, Calif.: Library
National Aeronautics and Space Administration, Washington, D. C.: Attn.: NPO (2) and Deutch, G.
Nuclear Materials and Equipment Corporation, Apollo, Penn.: B. Vondra
Sylvania Electric Products, Towanda, Penn.: M. MacInnis
Union Carbide Corporation, Lawrenceburg, Tenn.: W. Eatherly
United Nuclear Corporation, New Haven, Conn.: E. Gordon

EXTERNAL

M-3679, 41st Edition